TABLES OF PROPERTIES OF GASES

WITH DISSOCIATION THEORY AND ITS APPLICATIONS

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With diagrams

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PREFACE

The thermal properties of gases are used so extensively in engineering design that we feel justified in the publication of the present set of tables, which are based on the results of modern statistical thermodynamic analyses carried out by the various authorities to whom reference is made later. We agree with Heck [1] * when he states that it is preferable to use tables of the properties of gases against temperature rather than equations which show the relationship between the properties and temperature. The tables have accordingly been arranged to run from 400° F. abs. to 5400° F. abs., or, in a few cases to higher temperatures, by 100° F. intervals. Differences in the thermal properties are also printed so that by linear interpolation it is possible to evaluate these properties for any intermediate temperature. In practice this will be found considerably more convenient than the commonly adopted method of making use of equations for specific heats. In any case the latest specific heats cannot conveniently be expressed by any simple equation covering more than a limited range of temperature. In an article published by one of us in *Engineering*,[2] tables of thermal properties have already appeared but, as explained later, the properties presented in this volume have been built up from absolute zero temperature by regarding the gases as being in the hypothetical gaseous state throughout. This is of considerable assistance in dealing with problems on thermal equilibrium and enables the absolute entropy of a gas or mixture of gases to be calculated.

We trust that our explanation of the derivation of the tables and also of the modern approach to the theory of dissociation may prove of interest to engineers who have to deal with combustion problems. A valuable contribution on dissociation as affecting the engineer was made by Goodenough,[3] but at that time the accepted specific heats were inaccurate and in addition the simple evaluation of equilibrium constants by the free energy method had not yet been developed. We feel that this method should be more widely known by engineers and have, therefore, devoted space to its description and application.

We have much pleasure in acknowledging our indebtedness to Professor James Small for his helpful encouragement and criticisms. Our thanks are due also to the authorities of the University of Glasgow for the opportunities extended to us of doing this work and for the facilities we were privileged to use in connection with it.

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* References are to the bibliography, for which see p. 70.

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PRINCIPLES UPON WHICH THE TABLES ARE BASED

1. **Introduction.** The thermal properties of gases, which are presented in this volume, are based on the latest quantum specific heat values calculated by various physicists who have also checked them by spectroscopic analysis. The tables are applicable to the solution of ordinary engineering thermodynamic problems, some of which are given as examples later. In addition, however, they enable an accurate analysis of technical combustion processes, including dissociation effects, to be made. When the mixture of the products of combustion, found in the exhaust pipe of an internal combustion engine or in the flues of a steam boiler, is analysed, it is found generally to consist of the four gases CO_2, H_2O, O_2 and N_2. It has long been known, however, that a change in the physical condition of the mixture, such as an increase in temperature or decrease in pressure, tends to cause a splitting up of part of the CO_2 to CO and O_2 and of part of the H_2O to H_2 and O_2. Other changes may also occur such as the formation of OH and NO. These effects are known as dissociation, a name coined by Sainte-Clair Deville,(4) who spent the greater part of his life in its study. Later work was carried out by Gibbs,(5) Horstmann,(6) Haber,(7) Nernst (8) and van't Hoff.(9) This early work was not generally regarded as of importance to engineers until such authorities as Clerk,(10) Tizard and Pye,(11) Goodenough (12) and Schüle (13) had drawn attention to the effects of dissociation on technical combustion processes. For comparative purposes, modern values of specific heats, along with those suggested by various authorities two or three decades ago, for the technically important gases CO_2, H_2O, O_2 and N_2 have been plotted to a base of temperature in ° F. abs. in figs. 1, 2 and 3. It will be observed that the differences between the modern quantum values and the older ones are considerable, so that the errors in calculations involving the old specific heats may be large, and justify the publication of new thermal data and their application to combustion problems including dissociation. Since the work is intended for the use of engineers the thermal data are given in the form of tables in which the temperatures range from 400° F. abs. to 5400° F. abs. (in some cases to 9000° F. abs.) by 100° F. intervals.

2. **Molal Magnitudes.** It is convenient to express thermal magnitudes, of which internal energy and total heat are examples, in terms of the pound molecule or mol. The unit of mass is thus taken as m lb. where m is the molecular weight of a single gas or the apparent

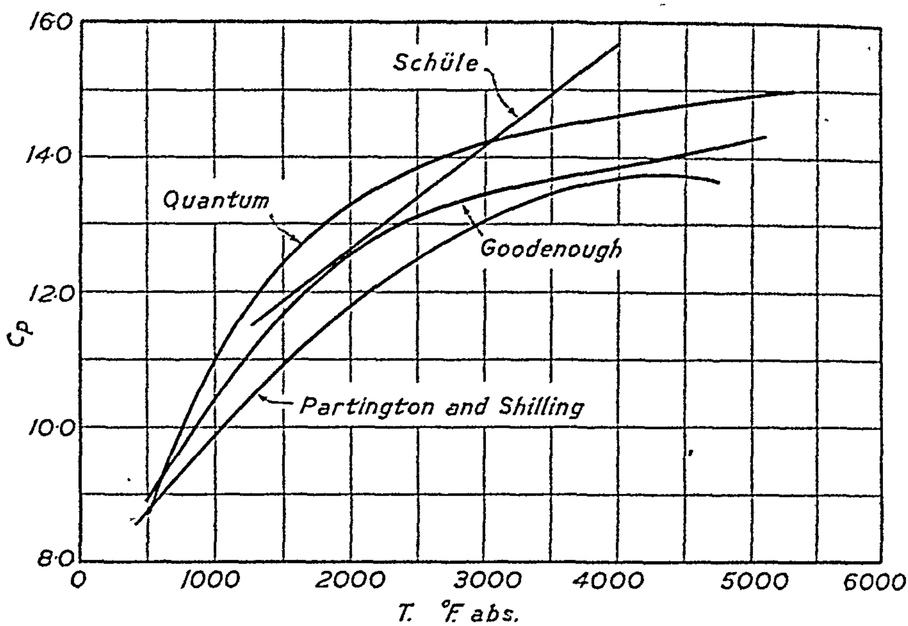

FIG. 1. Molecular specific heats of CO_2.

molecular weight of a mixture of gases. If the engineer desires to express any of these magnitudes per pound he has merely to divide them by the molecular weight when dealing with a single gas or by the apparent molecular weight when dealing with a mixture of gases. They are given at 100° F. temperature intervals and intermediate values are obtained by linear interpolation of the differences, which are also

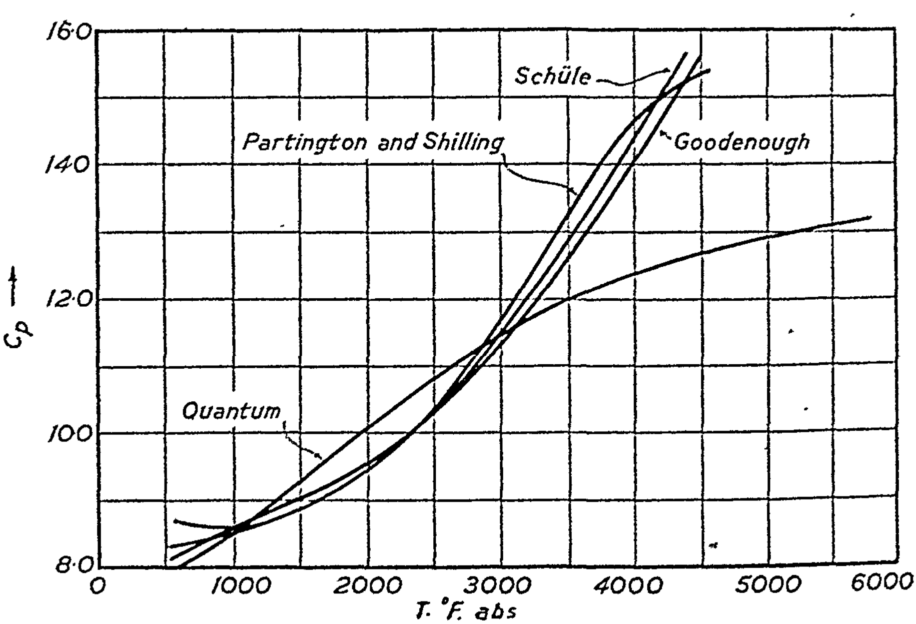

FIG. 2. Molecular specific heats of H_2O.

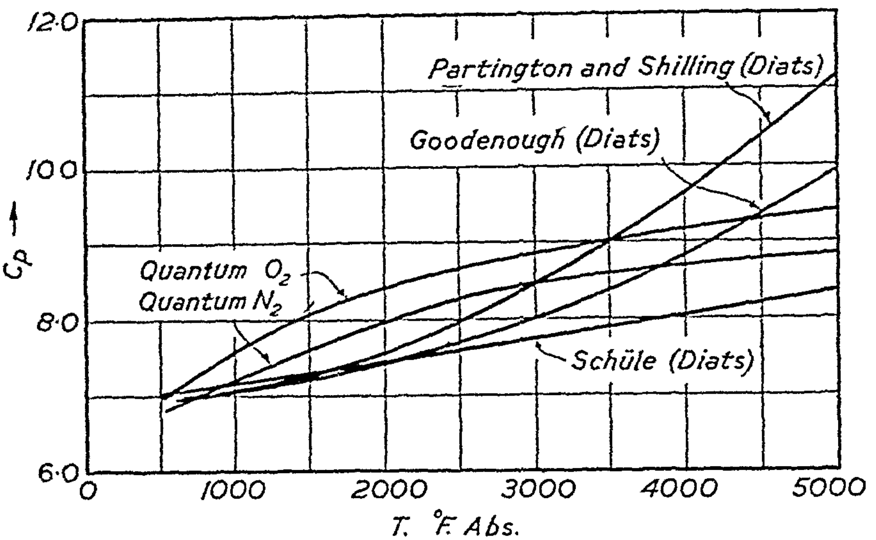

FIG. 3. Molecular specific heats of diatomics.

tabulated. The magnitudes and symbols listed in the tables are entropy, S; internal energy, E; total heat, H; lower heats of reaction at constant volume, H_v and constant pressure, H_p; equilibrium constant, K_p and a function of free energy expressed by $-\frac{F}{T}$. (See p. 25.)

3. **Entropy.** The entropy values are absolute, that is, they are all reckoned from absolute zero temperature. This has been rendered possible by the Nernst heat theorem,[14] which states that the entropy of all crystalline solids at absolute zero temperature is zero and that at very low temperatures, say, within 10 to 20° C. abs., the entropy values are small and, as the temperature is lowered to zero, they approach zero asymptotically. Since it is possible to measure specific heats of these crystalline solids between 10 and 20° C. abs. and since the Nernst heat theorem shows that extrapolition to absolute zero temperature is permissible, the absolute entropy values are calculable. Fig. 4 represents the entropy change of 1 gm. mol of oxygen when heated at a pressure of one atmosphere from zero absolute temperature to 298·1° C. abs. (25° C.). As shown by Debye,[15] the specific heat of crystalline solids at temperatures below 15° C. abs. is given by $C_p = kT^3$ and hence the entropy is given by

$$S = \int_0^T \frac{C_p\,dT}{T} = \int_0^T kT^2\,dT = \tfrac{1}{3}kT^3 \text{ or } \tfrac{1}{3}C_p.$$

It is thus possible to write down the entropy value when C_p is determined. For solid oxygen, $C_p = 0{\cdot}963$ at $T = 11{\cdot}75°$ C. abs. as given by

Johnson and Walker,(16) so that $S=0{\cdot}321$ E.U. (Entropy Unit), and $k=5{\cdot}95\times10^{-4}$. Between 0° C. abs. and 11·75° C. abs. the entropy values, as given by $\frac{1}{3}kT^3$, are as follows :

T	1	2	3	4
S	$1{\cdot}98\times10^{-4}$	$1{\cdot}58\times10^{-3}$	$5{\cdot}35\times10^{-3}$	$1{\cdot}27\times10^{-2}$
T	5	6	7	8
S	$2{\cdot}47\times10^{-2}$	$4{\cdot}28\times10^{-2}$	$6{\cdot}78\times10^{-2}$	$1{\cdot}012\times10^{-1}$
T	9	10	11·75	
S	$1{\cdot}444\times10^{-1}$	$1{\cdot}98\times10^{-1}$	$3{\cdot}21\times10^{-1}$	

The experimentally determined values of C_p between 12·97° C. abs. and 23·66° C. abs. enable the entropy values to be found by graphical integration. Thus, since the increment of entropy, as the temperature is increased from T to $T+\Delta T$, is given by

$$S=\int_T^{T+\Delta T}\frac{C_p\,dT}{T},$$

it is only necessary to plot values of $\frac{C_p}{T}$ to a base of temperature and integrate the area below the curve thus found to give the corresponding entropy increments. The total increment of entropy between 11·75° C. abs. and 23·66° C. abs., found in this way, is 1·697 E.U., and hence the entropy increase from A to B is $0{\cdot}321+1{\cdot}697=2{\cdot}018$ E.U. At 23·66° C. abs., as shown by BC in fig. 4, the first transition in the solid state occurs, the heat involved being 22·42 cals./gm. mol. The accompanying entropy increase is $\frac{22{\cdot}42}{23{\cdot}66}=0{\cdot}948$ E.U. At 43·76° C. abs. a second transition occurs (DE) and the increase in entropy between the two points C and D is again found graphically and amounts to 4·661 E.U. At this second transition point the heat of transition is 177·6 cals./gm. mol. giving $\frac{177{\cdot}6}{43{\cdot}76}=4{\cdot}058$ E.U. $=DE$ as the entropy increase. Between 43·76° C. abs. and 54·39° C. abs., i.e. between E and F the C_p values give the increase in entropy as 2·397 E.U. Up to 54·39° C. abs. the oxygen has remained in the solid state and at 54·39° C. abs. melting occurs, as shown by the line FG, the latent heat of fusion being 106·3 cals./gm. mol. so that the entropy increase is $\frac{106{\cdot}3}{54{\cdot}39}=1{\cdot}954$ E.U. Between 54·39° C. abs. and 90·13° C. abs., i.e. between G and H the oxygen remains in the liquid state and from the given C_p values the increase in the entropy is again found graphically and amounts to 6·462 E.U. Boiling occurs (HJ) at 90·13° C. abs., the latent heat being 1628·8 cals./gm. mol, so that the corresponding entropy increase is

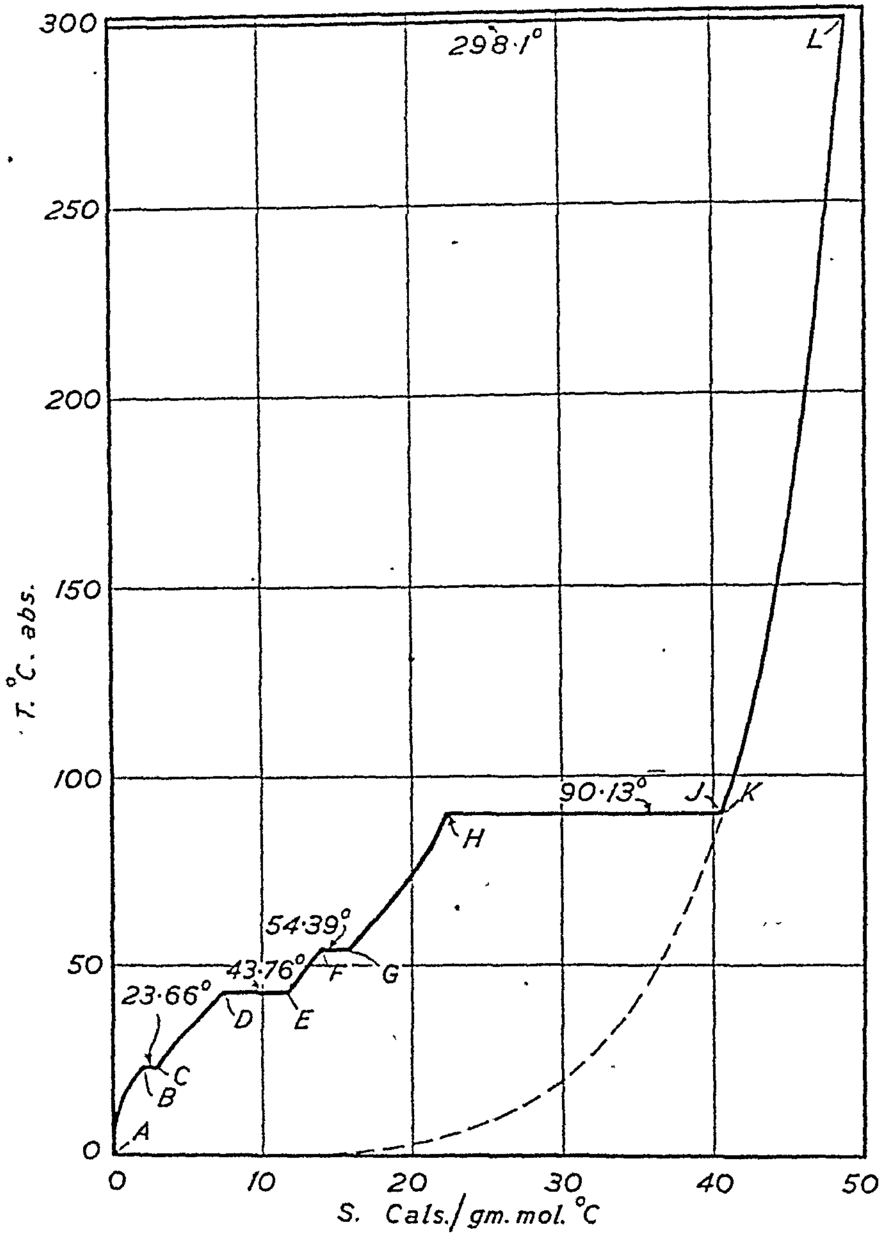

FIG. 4.

$\frac{1628 \cdot 8}{90 \cdot 13} = 18 \cdot 07$ E.U. The sum of the entropies taken over all the phases up to the point J amounts to 40·57 E.U. In order to bring the oxygen to what is called the standard state, which is necessary if the entropy is to be compared with spectroscopic data, the physicists apply a correction amounting to $\frac{27T_c^3P}{32T^3P_c}$, where T_c and P_c are the critical temperature

and critical pressure. This correction moves the state point from J to K but the scale of the diagram is such that the gap between the points does not show. The correction is deduced as follows. On the TS diagram (fig. 5) let J represent the state point of the actual gas at pressure p and temperature T, and K that of oxygen assumed to be reduced to the condition of a perfect gas having the characteristic equation $PV=RT$. If the pressure of both the actual and hypothetical gases is reduced, their state points approach one another until, in the limit when the pressure is zero, they actually coincide. This condition

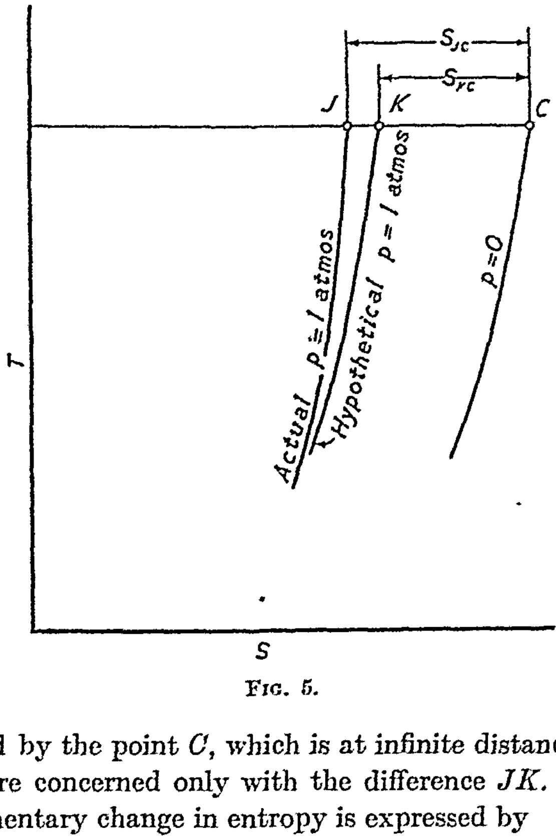

FIG. 5.

is represented by the point C, which is at infinite distance from J and K, but we are concerned only with the difference JK. Since for all gases an elementary change in entropy is expressed by

$$dS=\frac{C_p\,dT}{T}-\left(\frac{dV}{dT}\right)_P dP,$$

and since, in the case under consideration, $dT=0$, we have

$$dS=-\left(\frac{dV}{dT}\right)_P dP.$$

If, therefore, a gas is compressed isothermally from zero pressure to pressure P the change in entropy is

$$S=-\int_0^P\left(\frac{dV}{dT}\right)_P dP.$$

For the actual gas this is represented by the line CJ while for the perfect gas it is represented by the line CK.

Assuming that the actual gas obeys the modified Berthelot equation of state, i.e.

$$PV = RT\left[1 + \frac{9PT_c}{128P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right],$$

where T_c and P_c are the critical values of temperature and pressure, we have

$$\left(\frac{dV}{dT}\right)_P = \frac{R}{P}\left[1 + \frac{27}{32}\frac{PT_c^3}{P_cT^3}\right].$$

Hence

$$S_{JC} = CJ = -\int_0^P \frac{R}{P}\left[1 + \frac{27}{32}\frac{PT_c^3}{P_cT^3}\right] dP. \quad \text{..................(1)}$$

For the ideal gas, $PV = RT$ so that

$$\left(\frac{dV}{dT}\right)_P = \frac{R}{P},$$

and hence

$$S_{KC} = CK = -\int_0^P \frac{R}{P}\, dP. \quad \text{..........................(2)}$$

The value of the entropy change accompanying a change from the actual state to the ideal state is thus given by

$$JK = S_{JC} - S_{KC} = -\int_0^P \frac{27RT_c^3}{32T^3P_c}\, dP$$

$$= -\frac{27}{32}\frac{RT_c^3P}{T^3P_c}.$$

Hence
$$S^\circ = S + \frac{27RT_c^3P}{32T^3P_c}.$$

For oxygen $T_c = 154{\cdot}28^\circ$ C. abs. and $P_c = 49{\cdot}713$ atm. so that the correction is $\frac{27 \times 1{\cdot}9869 \times 154{\cdot}28^3 \times 1}{32 \times 90{\cdot}13^3 \times 49{\cdot}713} = 0{\cdot}17$ E.U. The entropy at the point K is thus 40·74 E.U.

The extension of the entropy curve upwards in fig. 4 from the point K to the point L, where the temperature is 298·1° C. abs., is again found by graphical integration using the experimentally determined values of C_p for this region. The increase in entropy found in this way is 8·28 E.U., so that the entropy of the oxygen at a temperature of 298·1° C. abs. and at a pressure of 1 atmosphere is 49·02 E.U.

Figure 6 shows the state changes for nitrogen again under a pressure of 1 atmosphere. It will be observed that there is only one transition in the solid state.

The advantage of expressing all the entropies of the gases dealt with

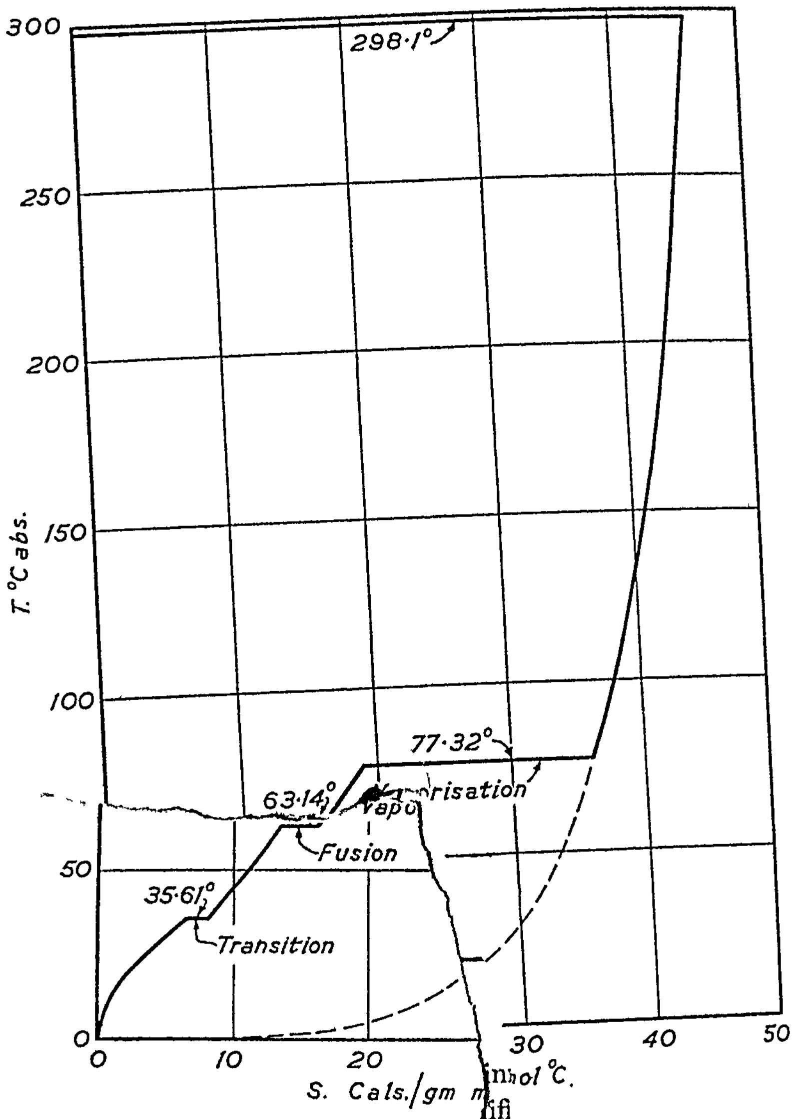

FIG. 6.

in combustion processes in the manner outlined above is that the entropies of a mixture of gases can now be correctly stated and if chemical reaction occurs between the gases the changes in absolute entropy between the products and the original mixture can be calculated. This gives a considerably simplified method of determining equilibria constants for reactions. The absolute entropy of a mixture of gases of known composition may be found at any pressure and temperature from the entropy values given in the tables as shown by the following example.

The products of combustion in the clearance volume of an engine cylinder have a total pressure of 400 lb./in.² abs. and a temperature

of 4000° F. abs. The percentage volumetric composition of the undissociated gas mixture is CO_2, 5·37; H_2O, 10·39; N_2, 73·72 and O_2, 10·52. It is required to find the absolute entropy of this gas mixture per pound mol.

The volumetric proportions are the same as the molal proportions. Figure 7 shows one pound mol of the mixture with the gases separated into proportional volumes as given by the analysis. The number of mols of the gases is as shown and if each gas is assumed to be at one atmosphere pressure and at a temperature of 4000° F. abs., the entropy of the mixture is given by ΣmS_T, where m is the number of mols and S_T the entropy of each gas. The tables give, for one mol of CO_2, H_2O, N_2 and O_2 at 4000° F. abs., the following values for S_T: 75·496; 64·624; 61·159 and 65·192, so that

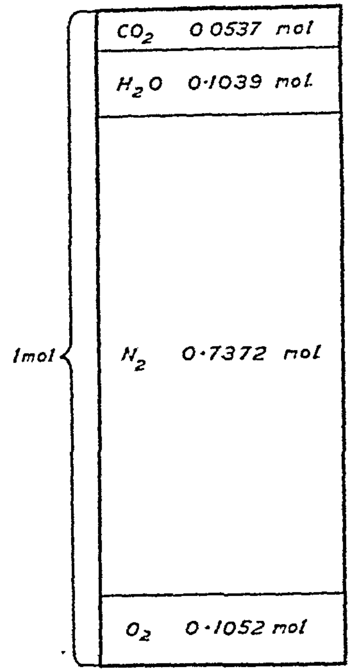

FIG. 7.

$$\Sigma mS_T = [0{\cdot}0537 \times 75{\cdot}496 + 0{\cdot}1039 \times 64{\cdot}624 + 0{\cdot}7372 \times 61{\cdot}159 + 0{\cdot}1052 \times 65{\cdot}192]$$
$$= 62{\cdot}713 \text{ E.U.}$$

In the actual gas mixture, however, each gas, instead of occupying its own volume at the total pressure, occupies the full volume (i.e. the volume of one pound mol) at its partial pressure and hence, due to the irreversible expansion from the volumes shown in the diagram to the final volume, each gas increases its entropy by an amount which is determined as shown below. In the deduction use is made of the idea of semipermeable walls. A substance which is capable of allowing one gas to pass through it and yet blocks the passage of other gases is said to be semipermeable. It is found that glowing platinum sheet permits hydrogen to pass freely through it, but not other gases, while a porous membrane, soaked in water, permits any gas which is soluble in water, such as ammonia, to flow freely through it and excludes gases which are insoluble in water, such as hydrogen. Up till now semipermeable walls have not been discovered for all gases but the discussion which follows is based on the conception of such materials existing, and enables an expression for the entropy increase, due to the expansion of a gas in a gas mixture, to be determined. Use will also be made of

the properties of semipermeable walls when discussing the maximum work of a reaction. (See p. 23.)

Consider two of the gases to be separated by semipermeable pistons as shown in fig. 8, i.e. the right hand piston is permeable to gas B while the left hand piston is permeable to gas A. The pressure between the two pistons in the position shown is $2p_a$ and if the left hand piston is held fast while the excess pressure is allowed to act on the right hand piston this will move to the right and external work will be available.

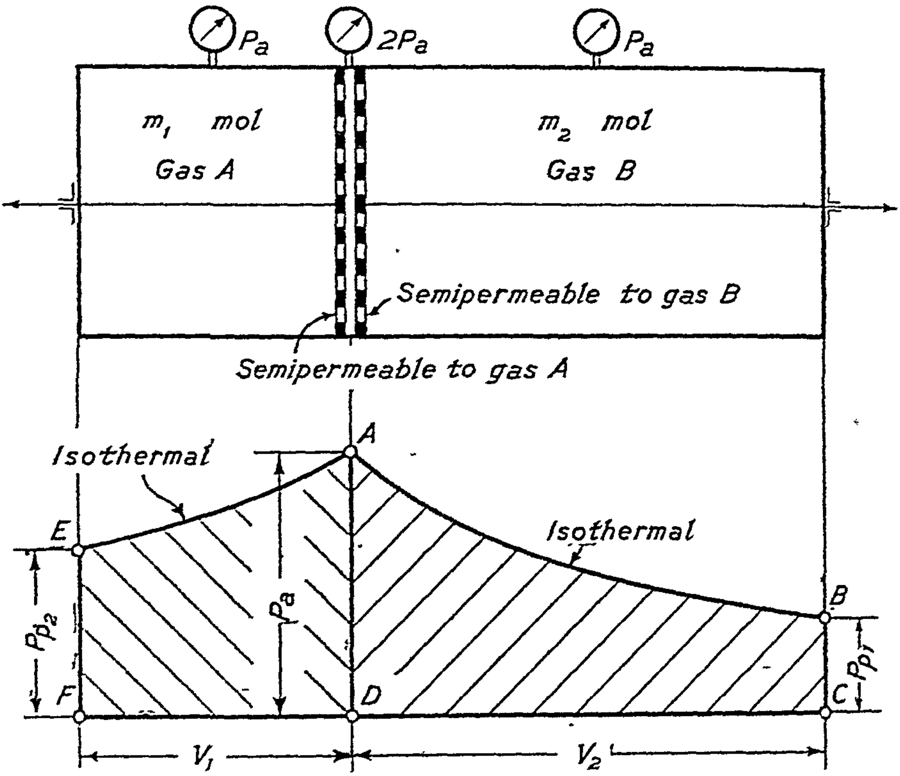

FIG. 8.

As the piston moves, gas B passes freely through its semipermeable wall so that it exerts no pressure on the piston. The gas A thus pushes this piston and performs work on it in the same way as would occur if the gas B were not present. With a slow enough motion of the piston the expansion may be made isothermal and reversible and the work performed is given by the area $ABCD$ which is equal to

$$\frac{RTm_1}{J}\log_e\frac{V_1+V_2}{V_1},$$

and since this equals the heat supplied at T the entropy change is

$$\frac{Rm_1}{J}\log_e\frac{V_1+V_2}{V_1}=\frac{Rm_1}{J}\log_e\frac{p_a}{p_{p_1}}.$$

If now the left hand piston is released gas B performs work on it, the amount being the same as would occur if the gas A were absent. This is given by the area $AEFD$ which is equal to

$$\frac{m_2RT}{J}\log_e\frac{V_1+V_2}{V_2}=\frac{m_2RT}{J}\log_e\frac{p_a}{p_{p_2}},$$

and the corresponding increase in entropy is

$$\frac{m_2R}{J}\log_e\frac{p_a}{p_{p_2}}.$$

If the total gas volume V_1+V_2 is equal to 1 mol we have

$$\frac{p_a}{p_{p_1}}=\frac{1}{m_1};\ \frac{p_a}{p_{p_2}}=\frac{1}{m_2},$$

or, in general,

$$\frac{p_a}{p_p}=\frac{1}{m},$$

and hence the entropy increase due to the expansion of any single gas is

$$\frac{mR}{J}\log_e\frac{p_a}{p_p}=\frac{mR}{J}\log_e\frac{1}{m}.$$

Hence for the mixture of gases of the example the increase is

$$\begin{aligned}
&\Sigma\frac{mR}{J}\log_e\frac{1}{m}\\
&\quad=1\cdot987\left[0\cdot0537\log_e\frac{1}{0\cdot0537}+0\cdot1039\log_e\frac{1}{0\cdot1039}\right.\\
&\qquad\left.+0\cdot7372\log_e\frac{1}{0\cdot7372}+0\cdot1052\log_e\frac{1}{0\cdot1052}\right]\\
&\quad=1\cdot987\times0\cdot854\\
&\quad=1\cdot697\text{ E.U.}
\end{aligned}$$

The total entropy at one atmosphere pressure and 4000° F. abs. is thus $62\cdot713+1\cdot697=64\cdot410$ E.U. The entropy is required, however, at 400 lb./in.^{2} abs. (27·21 atm.) and 4000° F. abs. On the PV and TS diagrams (fig. 9) the state point of the gas mixture at 1 atmosphere pressure would be represented by the point A. In changing its state to the point B, which is at the same temperature, any path may be chosen in order to calculate the entropy change. The simplest path to choose is the reversible isothermal at 4000° F. abs. passing through A and B. The heat rejected is

$$\begin{aligned}
&\frac{RT}{J}\log_e\frac{V_A}{V_B}=\frac{RT}{J}\log_e\frac{p_B}{p_A}\\
&\qquad=1\cdot987\times4000\log_e\frac{27\cdot21}{1}\text{ B.Th.U.}\\
&\qquad=1\cdot987\times4000\times3\cdot304\text{ B.Th.U.}
\end{aligned}$$

This is equal to the area $ABDC$ on the TS field so that the entropy decrease is $1{\cdot}987 \times 3{\cdot}304 = 6{\cdot}565$ E.U. The required entropy value of the gas mixture at the given conditions is thus $64{\cdot}410 - 6{\cdot}565 = 57{\cdot}845$ E.U.

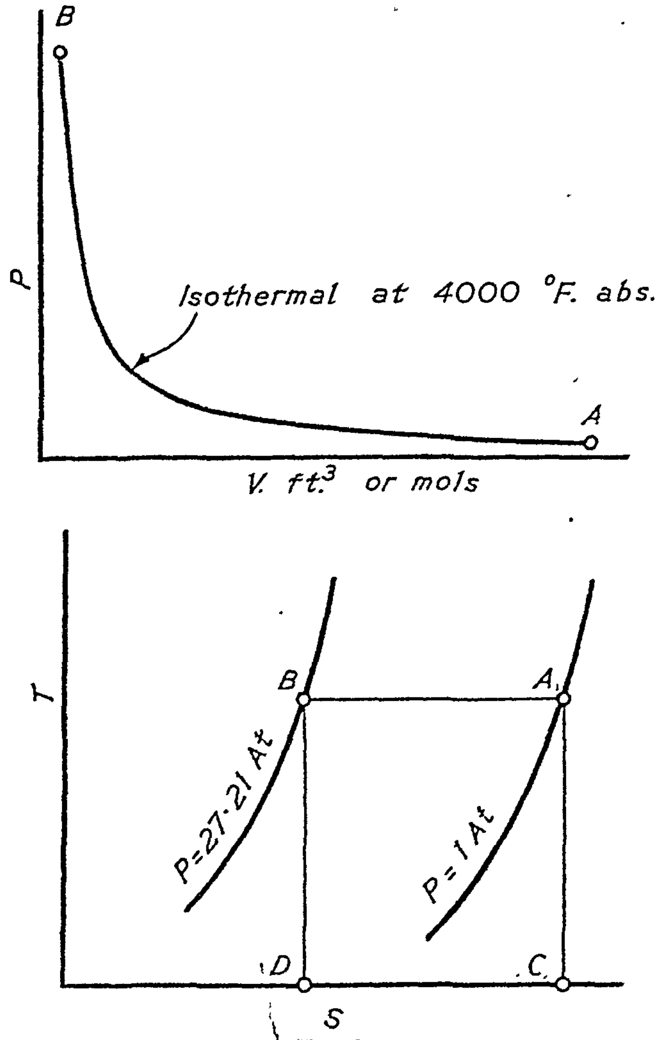

FIG. 9.

In determining the absolute entropy value of a gas or gaseous mixture the same procedure as outlined in the above example may be followed whatever the pressure, volume and temperature of the gas may be.

4. **Total Heat.** The total heat H of a gas is taken as the difference between the total heats of the gas at the temperature under consideration and the absolute zero temperature. If these total heats, which refer to the gas in the ideal or perfect gas state are denoted by $H_T{}^\circ$ and $H_0{}^\circ$ the total heats tabulated are equal to $H_T{}^\circ - H_0{}^\circ$. For a perfect

gas at absolute zero temperature H_0° is the same as the internal energy E_0° at that temperature so that the tabulated values of total heats are equal to $H_T^\circ - E_0^\circ$. The prefix 0 in these symbols denotes that the gas is in the ideal gaseous state. We have therefore for gases

$$H = H_T^\circ - E_0^\circ = \int_0^T C_p^\circ \, dT$$

where C_p° is the specific heat at constant pressure of the hypothetical gas already discussed in the previous paragraph. $(H_T^\circ - E_0^\circ)$ is thus equal to the area below the hypothetical gas curve shown on the TS

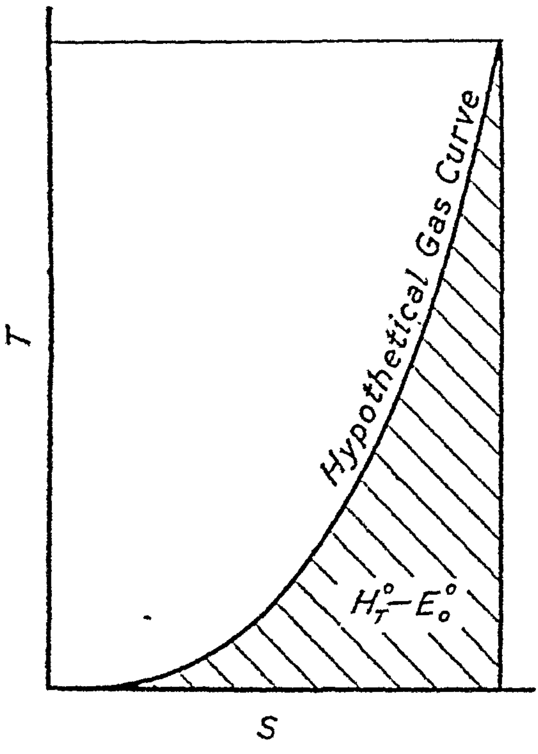

FIG. 10.

field in fig. 10 between 0° F. abs. and T° F. abs. A few skeleton values of $(H_T^\circ - E_0^\circ)$, at various temperature levels, are given in the original work of the physicists and it is from these that the values shown in the tables of this volume are deduced. Over limited ranges of temperature it is permissible to write

$$C_p = A + BT + CT^2,$$

where A, B and C are constants. Solving for the constants over one of these limited temperature ranges enable intermediate values of $(H_T^\circ - E_0^\circ)$ to be calculated. By covering the complete temperature

range from 400° F. abs. to the upper limits of 5400° F. abs. or 9000° F. abs. with these zones entirely satisfactory agreement with the original values was maintained.

5. **Internal Energy.** The internal energy, $E=(E_T{}^\circ-E_0{}^\circ)$, at any temperature T, is found from the total heat $(H_T{}^\circ-E_0{}^\circ)$ by means of the relationship

$$(E_T{}^\circ-E_0{}^\circ)=(H_T{}^\circ-E_0{}^\circ)-\frac{R}{J}T$$
$$=(H_T{}^\circ-E_0{}^\circ)-1{\cdot}9869T.$$

6. **Lower Heats of Reaction** (H_p). The engineer uses the word "lower" in referring to heats of reaction only when dealing with the combustion of hydrogen or fuels containing hydrogen, because at room temperature hydrogen is the only constituent forming a vapour which condenses. Since the physicists, however, have reduced the gases to the hypothetical gaseous state for which no condensation can occur, even when very low temperatures are considered, the heats of reaction for all gases must be referred to as "lower" heats of reaction.

The lower heat of reaction plays an important part in dissociation calculations and it has to be observed that the heat of reaction of a fuel depends upon the temperature at which the reaction occurs. Thus, if carbon monoxide is burned at constant pressure the heat given to the surroundings, under isothermal reaction conditions, is the constant pressure heat of reaction at room temperature. If, however, the reaction were to occur at some higher temperature the heat given up, i.e. the heat of the reaction, will have a different value from that at room temperature. This is due to the change which occurs in the difference of the total heats between the products and reactants as the temperature of the surroundings is altered. The point is made clear by considering the combustion of carbon monoxide. In burning one mol of carbon monoxide at a temperature of 600° F. abs. the heat of reaction is found to be 121794 B.Th.U. as given in the tables on page 93. The reaction proceeds in accordance with the reaction equation,

$$CO+\tfrac{1}{2}O_2=CO_2.$$

The sum of the total heats H_T-E_0 of the reactants, i.e. of 1 mol. of CO and $\frac{1}{2}$ mol of O_2 at 600° F. abs. is $4173+\frac{1}{2}\times4168=6257$ B.Th.U. and of the products (i.e. of 1 mol of CO_2), 4626 B.Th.U. The difference between the total heats of the reactants and products is thus $6257-4626=1631$ B.Th.U. and this makes the heat of reaction larger than it would have been had there been no difference in these total heats. If now the reaction proceeds at 5000° F. abs. the difference in the total heats of the reactants and the products is $40449+\frac{1}{2}\times42123-64132$

$= -2621$ B.Th.U. The heat of reaction is thus 2621 B.Th.U. less than it would have been if there were no difference between the total heats of the reactants and products. The heat of reaction of CO at 5000° F. abs. is thus less than that at 600° F. abs. by the amount $1631+2621 = 4252$ B.Th.U. and this equals the difference in the H_p values of CO as given in the tables at 600° F. abs. and 5000° F. abs. Since the values of $(H_T^\circ - E_0^\circ)$ are zero for all gases at 0° F. abs. there is no difference between the total heats of the reactants and products at this temperature and the heat of reaction, which is denoted by ΔE_0°, is the same as would be obtained at any other temperature provided the total heats of the reactants and the products were equal. Since, in almost all cases, there is a difference in the total heats and this difference is given by $\Delta(H_T^\circ - E_0^\circ)$, the true heat of reaction at any temperature is $\Delta E_0^\circ + \Delta(H_T^\circ - E_0^\circ)$. For CO, $\Delta E_0^\circ = 120163$ B.Th.U./lb. mol so that at 600° F. abs. $H_p = 120163 + 1631 = 121794$ B.Th.U./lb. mol as given in the tables. Similarly at 5000° F. abs. $H_p = 120163 - 2621 = 117542$ B.Th.U./lb. mol, as also given in the tables.

It frequently happens that it is not possible to find, by direct means, the heat of reaction of a fuel. In this case it is necessary to apply Hess's law, which states that the heat liberated by a reaction is independent of the path pursued between the initial and final states. If, for example, carbon is burned directly to form carbon dioxide the heat liberated is the same as would be the case if the carbon were first burned to carbon monoxide followed by burning of the carbon monoxide to carbon dioxide.

We shall illustrate the application of the law by determining the heat of reaction of benzene vapour (C_6H_6) at a temperature of 600° F. abs. The heat of reaction of benzene liquid can be found by first considering the liquid to be separated out to solid carbon and gaseous hydrogen. The carbon is then burned to CO_2 and the hydrogen to H_2O so that by applying Hess's law to these reactions we find the heat liberated in burning liquid benzene to gaseous CO_2 and gaseous H_2O. If benzene vapour had been burned instead of the liquid the latent heat required for evaporation of the liquid would not have been demanded from the fuel so that the heat of reaction of the vapour must be greater than that of the liquid by this amount. Finally, if all these operations occur at the usual temperature at which the heats are quoted, namely 537° F. abs. (25° C.), the heat of reaction at 600° F. abs. must be calculated by taking into account the difference in total heats between the reactants and products at 537° F. abs. and 600° F. abs.

Pitzer [17] has supplied the necessary data to enable a calculation of the heat of reaction of benzene vapour to be carried out on the above lines.

When splitting up liquid benzene to solid carbon and gaseous hydrogen, as shown by the reaction equation,

$$C_6H_{6(liq)} = 6C_{(s)} + 3H_{2(g)},$$

the heat liberated at 537° F. abs. is 20,160 B.Th.U./lb. mol. (See Parks.[18]) To find the heat of reaction of C burned to CO_2 we require the total heat of solid carbon, of gaseous O_2 and of gaseous CO_2 at 537° F. abs. These are given as 251, 2069 and 2240 cals./gm. mol while the heat of reaction at absolute zero temperature is 93949 cals./gm. mol. We thus have the heat of reaction for the combustion of carbon to carbon dioxide ($C + O_2 = CO_2$) at 298·1° C. abs. (25° C.) as

$$\begin{aligned} \Delta H &= 251 + 2069 + 93949 - 2240 \\ &= 94029 \text{ cals./gm. mol} \\ &= 169252 \text{ B.Th.U./lb. mol.} \end{aligned}$$

The table on p. 94 shows that the heat of reaction of $H_2 + \frac{1}{2}O_2 = H_2O$ at 537° F. abs. is 104009 B.Th.U./lb. mol.

From the reaction equation

$$C_6H_{6(liq)} + 7\tfrac{1}{2}O_2 = 6CO_2 + 3H_2O$$

we obtain the heat liberated at constant pressure

$$\begin{aligned} H_{p(537)} &= 20160 + 6 \times 169252 + 3 \times 104009 \\ &= 1347699 \text{ B.Th.U./lb. mol.} \end{aligned}$$

Matthews [10] gives the latent heat of benzene as

$$L = 107{\cdot}05 - 0{\cdot}15810\theta \text{ cals./gm.}$$

where θ is the temperature in ° C., so that at 25° C.

$$\begin{aligned} L &= 107{\cdot}05 - 3{\cdot}95 \\ &= 103{\cdot}1 \text{ cals./gm.} \\ &= 8045{\cdot}4 \text{ cals./gm. mol} \\ &= 14481 \text{ B.Th.U./lb. mol.} \end{aligned}$$

The value of H_p for benzene vapour is therefore (at 537° F. abs.)

$$14481 + 1347699 = 1362180 \text{ B.Th.U./lb. mol}$$

and at 600° F. abs. with

$$C_6H_{6(liq)} + 7\tfrac{1}{2}O_2 = 6CO_2 + 3H_2O$$

it becomes

$$\begin{aligned} H_{p(600)} &= 1362180 + (H_{600} - H_{537})_{C_6H_6} + 7\tfrac{1}{2}(H_{600} - H_{537})_{O_2} \\ &\quad - 6(H_{600} - H_{537})_{CO_2} - 3(H_{600} - H_{537})_{H_2O} \\ &= 1362180 + 1312 + 3359 - 3391 - 1508 \\ &= 1361952 \text{ B.Th.U./lb. mol.} \end{aligned}$$

The corresponding value at constant volume is

$$\begin{aligned} H_{v(600)} &= 1361952 + \tfrac{1}{2}RT/J \\ &= 1361952 + 596 \\ &= 1362548 \text{ B.Th.U./lb. mol,} \end{aligned}$$

since, under constant pressure conditions, there is an increase in volume amounting to $\frac{1}{2}$ mol per mol of fuel burned.

In the next paragraph the maximum work of a reaction is discussed and, as shown by Nernst, this maximum work is equal to the heat of reaction ΔE_0° at absolute zero temperature.

7. Maximum Work of Reaction and Equilibrium Constant. In applying the second law of thermodynamics to determine the maximum available work obtainable from a heat engine the discussion shows that this maximum is a function of the temperature range within which the working substance operates and further that this work is independent of the working substance. In the treatment, however, as usually given, only physical changes in the working substance are considered and all operations are regarded as reversible. When the combustion processes occurring in an engine are considered it would appear, at first sight, to be impossible to regard these as reversible, *and hence it would appear to be impossible to determine the value of* the maximum work attainable from a reaction. A conceivable method, however, can be pictured of a reaction process occurring in which all operations are reversible and from which work is obtainable, so that by applying the same arguments to the process as is normally done to reversible physical changes it is found that the work obtained from the reaction has a maximum value. This method, which enables an expression for the maximum work of reaction to be established, was suggested by van't Hoff and is illustrated by the van't Hoff equilibrium box.

In fig. 11 the vessel A is a reaction chamber of very large capacity maintained at constant temperature T by the surroundings. The reactants, taken in this case to be CO and O_2, are contained in the vessels B and C at the constant pressure p (in this preliminary discussion) and small quantities of these can be supplied, in the correct proportions for combustion, to the reaction chamber. Before entering the chamber, however, each gas is expanded isothermally in a motor to the partial pressure exerted by the gas in the reaction chamber. Work is thus rendered available, the amounts being, per mol of CO consumed,

$$pv \log_e \frac{p}{p_{CO}} \quad \text{and} \quad \tfrac{1}{2}pv \log_e \frac{p}{p_{O_2}},$$

where v is the volume of the pound mol, p_{CO} is the partial pressure of the CO and p_{O_2} the partial pressure of the O_2. As shown in the diagram the CO and O_2 gases are enabled to enter the reaction chamber because semipermeable walls, suitable for each gas, are fitted between the motors and the reaction chamber. The CO_2 formed by the reaction in vessel A escapes, as soon as it is formed, through the semipermeable

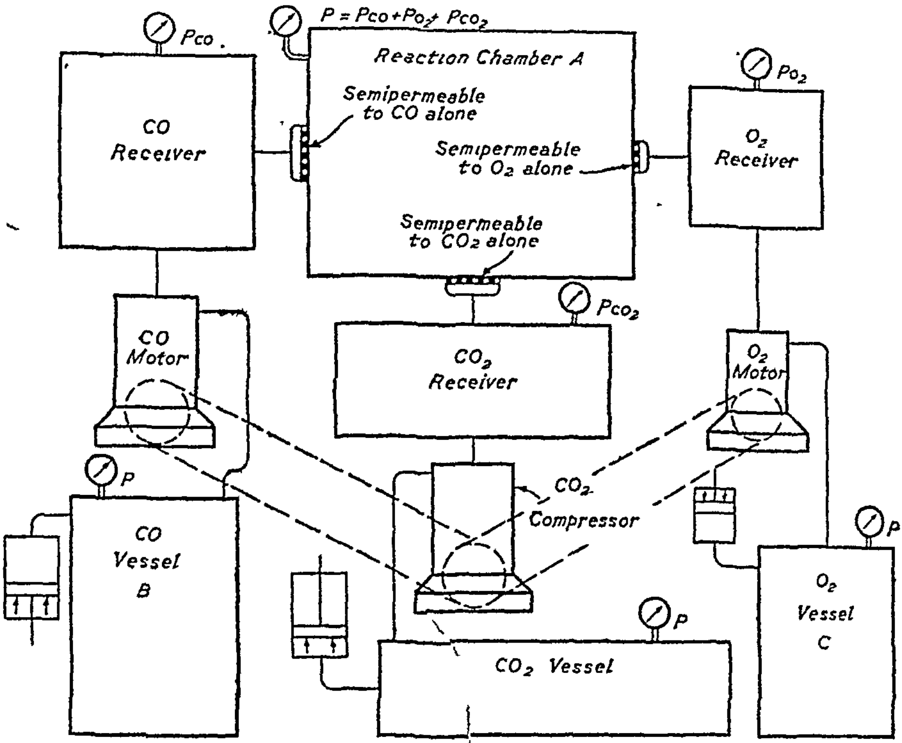

FIG. 11.

wall shown, to the CO_2 receiver, while the heat of the reaction is absorbed by the surroundings so that the process is isothermal and reversible. The discharged CO_2 is compressed isothermally from its pressure p_{CO_2} to the original pressure p of the reactants. The expenditure of work required for this is

$$pv \log_e \frac{p}{p_{CO_2}}.$$

The net gain in work is thus, in heat units,

$$\frac{pv}{J} \log_e \frac{p}{p_{CO}} + \tfrac{1}{2}\frac{pv}{J} \log_e \frac{p}{p_{O_2}} - \frac{pv}{J} \log_e \frac{p}{p_{CO_2}}$$
$$= \frac{RT}{J} \log_e \frac{p}{p_{CO}} \times \frac{p^{\frac{1}{2}}}{p_{O_2}^{\frac{1}{2}}} \times \frac{p_{CO_2}}{p}$$
$$= \frac{RT}{J} \log_e p^{\frac{1}{2}} \frac{p_{CO_2}}{p_{CO} \times p_{O_2}^{\frac{1}{2}}} \qquad \ldots\ldots(1)$$

All operations in the above reaction process are reversible since it is only necessary to return CO_2 to the reaction chamber and let heat flow in from the surroundings to enable the CO_2 to be split up to CO and O_2 and these are then returned to their original vessels. The work done, as given by equation (1), is thus a maximum for the reaction

$CO+\frac{1}{2}O_2=CO_2$ occurring at the constant temperature T and constant pressure p. If now, at this same temperature T and pressure p, a new set of conditions should exist in the reaction chamber so that the partial pressures of the reactants and products become p'_{CO}, p'_{O_2} and p'_{CO_2}, the same arguments shown above lead to the expression

$$\frac{RT}{J}\log_e p^{\frac{1}{2}}\frac{p'_{CO_2}}{p'_{CO}\times p'^{\frac{1}{2}}_{O_2}}$$

for the maximum work of reaction. Here also all operations are reversible so that this must equal the expression given in equation (1) as otherwise it would be possible to generate a continuous supply of energy merely by allowing the reaction showing the greater work to drive the one showing the lesser when this acts in the reverse direction. Hence

$$\frac{p_{CO_2}}{p_{CO}\times p^{\frac{1}{2}}_{O_2}}=\frac{p'_{CO_2}}{p'_{CO}\times p'^{\frac{1}{2}}_{O_2}}=K_p \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

is a constant known as the equilibrium constant. In any mixture of gases in which CO, O_2 and CO_2 are present alone or with other gases at the temperature T and total pressure p, the three gases CO, O_2 and CO_2 must, under equilibrium conditions, have partial pressures which satisfy the relationship given by equation (2), otherwise it would be possible for work to be done on or by any of these constituents and the mixture would not then be in equilibrium. If the reactants and products are not initially and finally all at the pressure p it becomes necessary to add or deduct the isothermal works of expansion or compression to or from equation (1) in order to find the maximum work of reaction. The value of K_p is, however, unaffected by these changes. It is customary to take the pressure p, appearing in equation (1), as one atmosphere so that the maximum work of reaction becomes $\frac{RT}{J}\log_e K_p$ with the partial pressures expressed in atmospheres. It has to be observed that this maximum work does not include the work done on or by the gases due to a difference between the sum of the mols of the reactants and the products. The cylinders shown attached to the receivers in fig. 11 indicate that for the combustion of CO with O_2 this work amounts to

$$\frac{pv}{J}+\frac{\frac{1}{2}pv}{J}-\frac{pv}{J}=\frac{1}{2}\frac{pv}{J}\text{ or }\frac{1}{2}\frac{RT}{J}.$$

8. **Free Energy.** In the last paragraph it was shown that the maximum work of a reaction is given by $\frac{RT}{J}\log_e K_p$, where K_p is the equilibrium constant and is a function of the partial pressures of the

reactants and products of the reaction. In order to calculate the value of K_p the following method due to Willard Gibbs and developed by Lewis will now be considered.

If the total heat, absolute entropy and absolute temperature of a hypothetically ideal gas be denoted by H_T, S_T and T we can write down a function F_T in terms of these as

$$F_T = H_T - TS_T.$$

Since H_T and TS_T are state functions it follows that this new function, known as the thermodynamic potential or free energy, is itself a state function. If now we denote this function for two states A and B of a substance by $(F_T)_A$ and $(F_T)_B$ we have, for an isothermal change,

$$(F_T)_A - (F_T)_B = \Delta F_T = \Delta H_T - \Delta TS_T = \Delta H_T - T\Delta S_T$$

where $\qquad \Delta H_T = (H_T)_A - (H_T)_B$ and $\Delta S_T = (S_T)_A - (S_T)_B$.

If the change is reversible $T\Delta S_T$ is the heat added and is denoted by Q say. We thus have

$$\Delta F_T = \Delta H_T - Q = \Delta E_T + \Delta PV - Q. \quad \text{......................(1)}$$

and if we regard the change as occurring at constant pressure as well as at constant temperature, $\Delta PV = P\Delta V$, which is the work done against the pressure P due to the change in volume ΔV. Rewriting equation (1) as

$$Q = \Delta E_T + (P\Delta V - \Delta F_T), \quad \text{............................(2)}$$

and comparing it with the energy law, i.e. heat supplied = change in internal energy + work done, we see that $-\Delta F_T$ represents the maximum work of the state change apart from that due to a change in volume. It is impossible for the maximum work obtainable to be any more or less than $-\Delta F_T$ and this applies to any reversible process in which the state changes from A to B. Thus, as quoted by Lewis and Randall, consider the action of aqueous sulphuric acid upon zinc under constant atmospheric pressure in a thermostat. Under normal conditions the reaction is highly irreversible and the only work performed is that due to the formation of hydrogen which has to expand against atmospheric pressure. If, however, the same substances are arranged as a galvanic cell in the thermostat with zinc as one electrode and a reversible hydrogen electrode as the other and if the two electrodes are connected externally to an electric motor so as to utilise the electrical energy now available, work will be performed and this will be a maximum if the opposing E.M.F. differs only by an infinitesimally small amount from that generated by the cell. Simultaneously with the production of electrical work zinc enters into solution at the zinc electrode and

hydrogen is evolved at the hydrogen electrode. The work performed will be a maximum because, by subsequent reduction of the opposing E.M.F. below that of the cell, hydrogen is consumed and zinc precipitated so that the process is reversible. Hence the net work available under electrical conditions is given by

$$(A_A - A_B) - P\Delta V$$

where $(A_A - A_B)$ is the external electrical work performed. From equation (2) the maximum work is $-\Delta F_T$ so that

$$-\Delta F_T = (A_A - A_B) - P\Delta V.$$

Hence for any process occurring at constant temperature and pressure,

$$-\Delta F_T = (F_T)_A - (F_T)_B \quad \text{..........................(3)}$$

is the maximum work which is available and applied usefully. For this reason F is called the free energy.

It has to be noted particularly that the work $-\Delta F$ of a reaction is not necessarily the same as the heat of the reaction. As shown by Nernst the two are equal at absolute zero temperature and will also be equal at any given temperature if the heat capacity, reckoned from absolute zero, of the reactants is the same as that of the products and if the sum of the entropies of the reactants is the same as that of the products. It has been shown that the maximum work of a reaction is given by the change in free energy, but no reference has been made as to how this change is computed. Since the thermal magnitudes are reckoned from absolute zero temperature, the change in free energy for a reaction must include the change in free energy at absolute zero temperature and this is equal to $-\Delta E_0$. Hence the maximum work is given by the expression

$$-\Delta E_0 - \Delta(F_T - E_0)$$

and, since this is the same as the work available in the van't Hoff equilibrium box, we have

$$\frac{RT}{J}\log_e K_p = -\Delta E_0 - \Delta(F_T - E_0)$$

or

$$\frac{R}{J}\log_e K_p = -\Delta E_0/T - \Delta(F_T - E_0)/T.$$

The function $-\dfrac{(F_T - E_0)}{T} = -\dfrac{F}{T}$ is given in the tables as also ΔE_0 so that the value of $\log_e K_p$ is calculable. As an example, we choose the combustion of carbon monoxide with oxygen to form carbon dioxide at a temperature of 600° F. abs. The sum of the free energy functions of the reactants CO and $\frac{1}{2}O_2$ is $-41{\cdot}149 - \frac{1}{2} \times 42{\cdot}871 = -62{\cdot}585$

B.Th.U./lb. mol × ° F. while the free energy function of the CO_2 is $-44{\cdot}394$ B.Th.U./lb. mol × ° F. The change is thus

$$-62{\cdot}585+44{\cdot}394=-18{\cdot}191 \text{ B.Th.U./lb. mol} \times {}^\circ\text{F.}$$

Also the heat of reaction $-\Delta E_0$ of CO at 0° F. abs. is given as 120163 B.Th.U./lb. mol so that

$$-\frac{\Delta E_0}{T}=120163/600=200{\cdot}272 \text{ B.Th.U./lb. mol.} \times {}^\circ\text{F.}$$

We thus have

$$\frac{R}{J}\log_e K_p=200{\cdot}272-18{\cdot}191=182{\cdot}081,$$

and hence

$$\begin{aligned}\log_{10} K_p &= 182{\cdot}081/1{\cdot}987 \times 2{\cdot}303\\ &= 39{\cdot}80\end{aligned}$$

and

$$K_p=6{\cdot}3096 \times 10^{39}$$

as given in the tables.

EXAMPLES ON THE USE OF THE TABLES

EXAMPLE 1

Flue gases leave a boiler at a temperature of 600° F. and have the fractional composition: O_2, 0·098; N_2, 0·799; CO_2, 0·098 and H_2O, 0·005. This composition gives an apparent molecular weight of 29·91. It is required to find the heat given up by 1 lb. of these gases if cooled to a temperature of 80° F. at constant pressure. Assume that the H_2O remains in the gaseous state down to 80° F.

The total heat of the mixture has to be calculated at 600° F. (1060° F. abs.) by multiplying the number of mols of each constituent by its total heat at 1060° F. abs. and summing the results so obtained. This procedure has to be repeated at 80° F. (540° F. abs.). The difference between these quantities then gives the heat liberated.

Arranging the work in tabular form we have at $T=1060$° F. abs.:

Gas	Vol. or No. of mols (m)	H_{1060}	mH_{1060}
O_2	0·098	7549	739·8
N_2	0·799	7416	5925·5
CO_2	0·098	9378	919·0
H_2O	0·005	8636	43·2
			$\Sigma mH_{1060}=7627{\cdot}5$

and at $T=540°$ F. abs. :

Gas	m	H_{540}	mH_{540}
O_2	0·098	3751	367·6
N_2	0·799	3753	2998·7
CO_2	0·098	4088	400·6
H_2O	0·005	4318	21·6
		$\Sigma mH_{540}=3788{\cdot}5$	

The difference in total heat is thus

$$7627{\cdot}5-3788{\cdot}5=3839{\cdot}0 \text{ B.Th.U./lb. mol}$$

and since the apparent molecular weight of the flue gases is 29·91 the heat given up per pound is

$$3839{\cdot}0/29{\cdot}91=128{\cdot}4 \text{ B.Th.U.}$$

EXAMPLE 2

The products of combustion of a petrol engine, supplied with 20 per cent. excess air, have the following volumetric analysis : N_2, 0·7466 ; O_2, 0·0329 ; CO_2, 0·1084 ; H_2O, 0·1121. This gives an apparent molecular weight of 28·75 and gas constant $R=53{\cdot}70$. If the tempera-

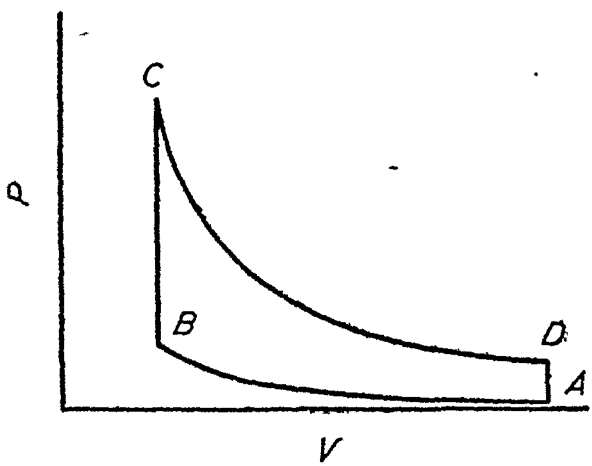

FIG. 12.

ture of the charge at the beginning of compression is 100° F. and the compression ratio of the engine is 5, it is required to find the ideal thermal efficiency of the engine. The calorific value of the petrol used is 20,300 B.Th.U./lb. and its gravimetric composition is 85·3 per cent. carbon and 14·7 per cent. hydrogen.

In determining the ideal efficiency, it is permissible to assume that the working substance consists of the products of combustion through-

out the complete cycle. The ideal cycle consists of isentropic compression (AB in fig. 12), constant volume burning (BC), isentropic expansion (CD) and constant volume cooling (DA).

In order to find the temperature at B, a value is first assumed and if correct, it will be found that the entropy at B is the same as at A. If this agreement is not obtained the process is repeated until the condition is satisfied.

Denoting the pressures at A and B by p_A and p_B, we have, for the entropy at A,

$$S_A = \Sigma m (S_T)_A + \Sigma m \frac{R}{J} \log_e \frac{1}{p_p} + \frac{R}{J} \log_e \frac{1}{p_A}, \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where, for each constituent, m is the number of mols, $(S_T)_A$ is the entropy at a pressure of 1 atmosphere and p_p the partial pressure (in atmospheres) when the pressure of the mixture is 1 atmosphere. p_A is the total pressure (in atmospheres) of the gas mixture at A. The first term on the right of equation (1) represents the entropy of the gas mixture with each constituent at a pressure of 1 atmosphere (as given by the tables). The second term is the correction necessary to bring the mixture to a pressure of 1 atmosphere so that each constituent is subjected to a reduction in pressure from 1 atmosphere to its own partial pressure p_p. The third expression gives the necessary correction to bring the mixture from 1 atmosphere pressure to p_A the pressure at A.

In the same way the entropy at B is given by the expression

$$S_B = \Sigma m (S_T)_B + \Sigma m \frac{R}{J} \log_e \frac{1}{p_p} + \frac{R}{J} \log_e \frac{1}{p_B} \quad \ldots\ldots\ldots\ldots\ldots(2)$$

The second terms on the right of equations (1) and (2) are equal so that the difference in entropy between the state points A and B is given by the expression

$$S_A - S_B = \Sigma m (S_T)_A - \Sigma m (S_T)_B + \frac{R}{J} \log_e \frac{p_B}{p_A};$$

but

$$\frac{p_B}{p_A} = r_c \frac{T_B}{T_A}$$

where r_c is the compression ratio, $\frac{V_A}{V_B}$.

This gives

$$S_A - S_B = \Sigma m (S_T)_A - \Sigma m (S_T)_B + \frac{R}{J} \log_e r_c \frac{T_B}{T_A}$$

$$= \Sigma m (S_T)_A + \frac{R}{J} \log_e \frac{r_c}{T_A} - \Sigma m (S_T)_B + \frac{R}{J} \log_e T_B. \quad \ldots\ldots\ldots(3)$$

The first two terms on the right remain constant for all assumed values of T_B so that it is advisable to determine their sum independently and equate this to the last two terms. Arranging the work in tabular form, we have

Gas	Vol. or mols (m)	S_{560}	mS_{560}
N_2	0·7466	46·067	34·41
O_2	0·0329	49·299	1·62
CO_2	0·1084	51·452	5·58
H_2O	0·1121	45·452	5·09
		$\Sigma m\dot{S}_{560}=46·70$	

The second term in equation (3) is $\frac{R}{J}\log_e\frac{r_c}{T_A}$

$$=1·986\times 2·303\log_{10}5/560$$
$$=-9·371 \text{ E.U.}$$

The first two terms in equation (3) are thus equal to $46·70-9·37=37·33$ E.U. and this must equal

$$\Sigma m(S_T)_B-\frac{R}{J}\log_e T_B.$$

For $\Sigma m(S_T)_B$ it is convenient again to arrange the work in tabular form with an assumed temperature of $T_B=1000°$ F. abs.:

Gas	m	S_{1000}	mS_{1000}
N_2	0·7466	50·158	37·44
O_2	0·0329	53·533	1·76
CO_2	0·1084	57·284	6·21
H_2O	0·1121	50·257	5·63
		$\Sigma mS_{1000}=51·04$	

and $\frac{R}{J}\log_e T_B=1·986\times 2·303\log_{10}1000$

$$=13·72.$$

Hence
$$\Sigma mS_{1000}-\frac{R}{J}\log_e T_B$$
$$=51·04-13·72$$
$$=37·32$$

as against 37·33 for the first two terms so that the assumed temperature for T_B of 1000° F. abs. may be accepted. The corresponding value of the internal energy E_2 at the point B is found by multiplying the number of mols of each constituent in the products by its internal

energy value as given in the tables at 1000° F. abs. and summing the products. It is convenient to carry out the calculation in tabular form as follows:

Gas	m	E_{1000}	mE_{1000}
N_2	0·7466	4998	3731·5
O_2	0·0329	5104	167·9
CO_2	0·1084	6722	728·7
H_2O	0·1121	6130	687·2
		$E_2 = \Sigma mE_{1000} = 5315·3$	

In order to find the temperature T_3 at the end of the constant volume burning period, its value is first assumed and the internal energy E_3 of the products calculated. If this is found to equal $E_2 + Q$, i.e. the internal energy at the point B plus the heat added per lb. mol, then the assumed temperature is correct. If not, the process is repeated until the condition is satisfied. From the data supplied in the statement of the problem it can be shown that the weight of the products of combustion per lb. of petrol is 18·85 lb. so that the heat added is

$$Q = 20{,}304 \times 28·75/18·85 = 30964 \text{ B.Th.U./lb. mol.}$$

If now we assume T_3 to be 5200° F. abs. the value of E_3 is found as follows:

Gas	m	E_{5200}	mE_{5200}
N_2	0·7466	31560	23563
O_2	0·0329	33680	1108
CO_2	0·1084	56796	6156
H_2O	0·1121	45907	5146
		$E_3 = \Sigma mE_{5200} = 35973$	

Since this is less than the required value of 36279 the assumed temperature of 5200° F. abs. for T_3 is too low. By further trial and error the required value of T_3 is found to be 5238° F. abs. and the corresponding value of E_3 is 36280 B.Th.U./lb. mol.

The entropy of the gaseous mixture at C must be the same as at D so that the temperature at D has to be found, by trial and error, until this condition is satisfied. The calculation is similar to that carried out during compression so that the detailed method does not require to be repeated. It is found that the required temperature at D is 3500° F. abs. and the corresponding value of E_D is 22683 B.Th.U./lb. mol. At $T_A = 560°$ F. abs. the value of E_A is 2887 B.Th.U./lb. mol.

The efficiency is given by the expression

$$\eta = \frac{(E_C - E_B) - (E_D - E_A)}{(E_C - E_B)}$$
$$= 1 - \frac{(E_D - E_A)}{Q}$$
$$= 1 - \frac{22683 - 2887}{30964}$$
$$= 0{\cdot}361.$$

EXAMPLE 3

A nozzle is supplied with air at a pressure of 62·0 lb./in.^{2} abs. and temperature of 1600° F. abs. If the rate of air flow is 10 lb./sec. and the pressure at outlet from the nozzle is 14·7 lb./in.^{2} abs., find the throat and exit areas. Assume that expansion to the throat is isentropic and that the frictional loss, for the complete expansion between inlet to and outlet from the nozzle is 15 per cent. of the isentropic heat drop. Assume also that the composition of the air by volume is O_2, 21 per cent. and N_2, 79 per cent. so that the molecular weight is 28·84 and the gas constant is 53·53.

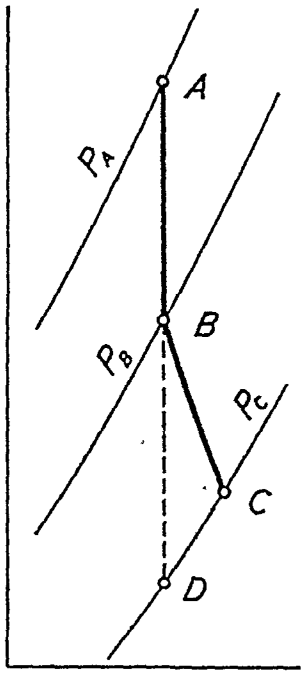

FIG. 13.

It is necessary to find the mean isentropic index of expansion γ between the nozzle inlet and throat. The critical pressure ratio (r_c) is given by

$$r_c = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma-1}} \qquad \text{...........................(1)}$$

and if γ is taken provisionally as 1·4 we have $r_c = 0{\cdot}53$ so that the throat pressure is nearly $0{\cdot}53 \times 62{\cdot}0 = 32{\cdot}9$, say 33 lb./in.^{2} abs. and the corresponding temperature is $T_B = T_A r_c^{\frac{\gamma-1}{\gamma}} = 1334{\cdot}5°$ F. abs. The mean value of γ between A and B in fig. 13 (where A represents the state point of the air at the nozzle inlet and B at the throat) can be found, when T_B is known, from the relationship

$$T_A/T_B = (p_A/p_B)^{\frac{\gamma-1}{\gamma}} \qquad \text{...............................(2)}$$

and the critical pressure ratio can then be found from equation (1). The entropy of 1 mol of air at A is given by the expression (see p. 30)

$$\Sigma m\, S_{1600} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_A},$$

where m is the fractional number of mols of the gases, oxygen and nitrogen. The corresponding expression for the entropy at B is

$$\Sigma m\, S_{1334\cdot5} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_B}.$$

Since the entropies at A and B are equal, we have

$$\Sigma m\, S_{1600} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_A}$$
$$= \Sigma m\, S_{1334\cdot5} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_B},$$

so that

$$\Sigma m\, S_{1600} - \Sigma m\, S_{1334\cdot5} = \frac{R}{J} \log_e \frac{p_A}{p_B}.$$

Since m for O_2 is 0·21 and for N_2, 0·79, we have

$$0\cdot21\,(S_{1600})_{O_2} + 0\cdot79\,(S_{1600})_{N_2} - 0\cdot21\,(S_{1334\cdot5})_{O_2} - 0\cdot79\,(S_{1334\cdot5})_{N_2}$$
$$= \frac{R}{J} \log_e \frac{62\cdot0}{p_B}$$

from which p_B is calculable.

From the tables $(S_{1600})_{O_2} = 57\cdot240$; $(S_{1600})_{N_2} = 53\cdot617$; $(S_{1334\cdot5})_{O_2} = 55\cdot769$ and $(S_{1334\cdot5})_{N_2} = 52\cdot252$.

Hence

$$\frac{R}{J} \log_e \frac{62\cdot0}{p_B} = 0\cdot21\,(57\cdot240 - 55\cdot769) + 0\cdot79\,(53\cdot617 - 52\cdot252)$$
$$= 1\cdot3874;$$
$$\log_{10} \frac{62\cdot0}{p_B} = \frac{1\cdot3874}{1\cdot987 \times 2\cdot303} = 0\cdot30336;$$
$$p_B = 30\cdot833.$$

It has to be remembered that these values of $p_B = 30\cdot833$ lb./in.^{2} abs. and $T_B = 1334\cdot5°$ F. abs. are not the true values at the throat, but they are on the isentropic curve passing through A and so the mean index γ found from them must be nearly correct.

From equation (2) we now have

$$\frac{1600}{1334\cdot4} = \left(\frac{62\cdot0}{30\cdot833}\right)^{\frac{\gamma-1}{\gamma}}$$

from which $\gamma = 1\cdot351$.

The critical pressure ratio is thus

$$r_c = \left(\frac{2}{1\cdot351}\right)^{\frac{1\cdot351}{0\cdot351}}$$
$$= 0\cdot537$$

so that the critical pressure is $0\cdot537 \times 62\cdot0$

$$= 33\cdot30 \text{ lb./in.}^2 \text{ abs.}$$

The corrected value of T_B is now given by

$$T_B = 1600\left(\frac{33\cdot30}{62\cdot0}\right)^{\frac{0\cdot351}{1\cdot351}}$$
$$=1361\cdot4^\circ \text{ F. abs.}$$

The specific volume at the throat is given by

$$v_B = RT/144p = 53\cdot53\times1361\cdot4/144\times33\cdot30$$
$$=15\cdot20 \text{ ft.}^3\text{/lb.}$$

In order to find the throat area, the throat velocity is required. This is found from the isentropic heat drop $(\Delta_s)_{AB}$ between A and B, i.e. between the temperatures 1600° F. abs. and 1361·4° F. abs.

Thus $(\Delta_s)_{AB}$

$$=0\cdot21(H_{1600}-H_{1361\cdot4})_{O_2}+0\cdot79(H_{1600}-H_{1361\cdot4})_{N_2}$$
$$=0\cdot21(11842-9909)+0\cdot79(11420-9622)$$
$$=1827 \text{ B.Th.U./lb. mol.} = 63\cdot35 \text{ B.Th.U./lb.}$$

The velocity at the throat is given by

$$V_B = 223\cdot8\sqrt{63\cdot35}$$
$$1781\cdot2 \text{ ft./sec.}$$

The throat area is now given by

$$A_B = 144mv_B/V_B$$
$$=144\times10\times15\cdot20/1781\cdot2$$
$$=12\cdot28 \text{ in.}^2$$

For the complete expansion through the nozzle it is necessary to find the isentropic heat drop from inlet to outlet. This is determined in the same way as before when finding the throat area, but in this case the lower pressure is known, so that the entropy equation is, with T_D equal to the temperature at the nozzle outlet,

$$0\cdot21\{(S_{1600})_{O_2}-(S_{T_D})_{O_2}\}+0\cdot79\{(S_{1600})_{N_2}-(S_{T_D})_{N_2}\}$$
$$=\frac{R}{J}\log_e 62\cdot0/14\cdot7$$

or
$$0\cdot21(S_{1600})_{O_2}+0\cdot79(S_{1600})_{N_2}-\frac{R}{J}\log_e 62\cdot0/14\cdot7$$
$$=0\cdot21(S_{T_D})_{O_2}+0\cdot79(S_{T_D})_{N_2}. \qquad \text{.................................(3)}$$

The expression on the left of equation (3) is first determined, after which the temperature T_D is assumed and, if correct, it will be found that the equation is satisfied, otherwise the procedure is repeated until agreement is obtained.

Inserting the values $(S_{1600})_{O_2}=57\cdot240$ and $(S_{1600})_{N_2}=53\cdot617$, as given by the tables, on the left-hand side of equation (3) we have

$$0\cdot21\times57\cdot240+0\cdot79\times53\cdot617-1\cdot986\times2\cdot303\log_e 62\cdot0/14\cdot7$$
$$=12\cdot021+42\cdot357-2\cdot859$$
$$=51\cdot52 \text{ E.U.}$$

If we assume $T_D = 1100°$ F. abs. the tables give $(S_{1100})_{O_2} = 54{\cdot}260$ and $(S_{1100})_{N_2} = 50{\cdot}842$ so that the right-hand side of equation (3) is then

$$\begin{aligned} &0{\cdot}21 \times 54{\cdot}260 + 0{\cdot}79 \times 50{\cdot}842 \\ &= 51{\cdot}56 \text{ E.U.} \end{aligned}$$

as against 51·52 E.U. for the left-hand side, so that the assumed value of $T_D = 1100°$ F. abs. may be accepted. The isentropic heat drop between 1600° F. abs. and 1100° F. abs. is now found from

$$\begin{aligned} (\Delta_s)_{AD} &= 0{\cdot}21\,(H_{1600} - H_{1100})_{O_2} + 0{\cdot}79\,(H_{1600} - H_{1100})_{N_2} \\ &= 0{\cdot}21\,(11842 - 7855) + 0{\cdot}79\,(11420 - 7704) \\ &= 3773 \text{ B.Th.U./lb. mol.} \end{aligned}$$

The net heat drop is 0·85 of $(\Delta_s)_{AD}$, so that we have

$$0{\cdot}85 \times 3773 = 0{\cdot}21\,(H_{1600} - H_{T_C})_{O_2} + 0{\cdot}79\,(H_{1600} - H_{T_C})_{N_2} \quad \text{.......(4)}$$

where T_C is the actual temperature at the nozzle outlet.

T_C has to be guessed so as to satisfy equation (4). Trying $T_C = 1200°$ F. abs. we have

$$\begin{aligned} 0{\cdot}85 \times 3773 &= 0{\cdot}21\,(11842 - 8631) + 0{\cdot}79\,(11420 - 8430) \\ 3207 &= 3036, \end{aligned}$$

so that agreement is not obtained.

The heat drop calculated on the right-hand side of the equation is too low and therefore the guessed temperature is too high. By further trial and error it is found that the correct value of T_C is 1177° F. abs., so that the specific volume of the air at the nozzle exit is

$$\begin{aligned} v_c &= 53{\cdot}53 \times 1177/144 \times 14{\cdot}7 \\ &= 29{\cdot}77 \text{ ft.}^3/\text{lb.} \end{aligned}$$

and the exit velocity is

$$\begin{aligned} V_C &= 223{\cdot}8\sqrt{111{\cdot}2} \\ &= 2360 \text{ ft./sec.} \end{aligned}$$

since the net heat drop per pound of air is

$$3207/28{\cdot}84 = 111{\cdot}2 \text{ B.Th.U.}$$

The exit area is thus given by

$$\begin{aligned} A_C &= 144 \times 10 \times 29{\cdot}77/2360 \\ &= 18{\cdot}16 \text{ in.}^2 \end{aligned}$$

Example 4

A closed vessel of 1 ft.³ internal capacity contains air at a temperature of 4000° F. abs. and pressure of 1 atmosphere. If the air is cooled at constant volume to a temperature of 520° F. abs. which is the temperature of the surroundings and the heat thus liberated is used as a source

for a perfect heat engine, find the maximum attainable work. Neglect dissociation effects and assume that the air contains 21 per cent. of oxygen and 79 per cent. of nitrogen by volume.

The initial state point of the air is represented by the point A (fig. 14) on the TS diagram and AB is a constant volume curve with B on the temperature level of 520° F. abs. At any temperature level T

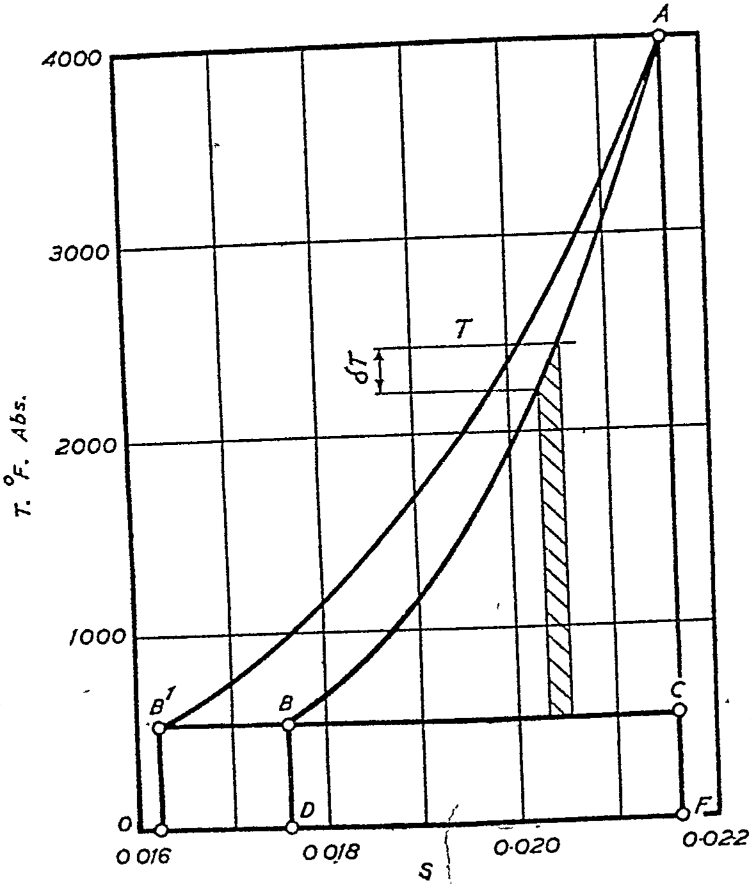

FIG. 14.

the elementary maximum work is that given by the Carnot engine cycle when the heat source is at T and the temperature drop is δT, i.e. it is given by the elementary area shown shaded in the TS diagram. Hence for the complete cooling from A to B the maximum available work is given by the area ABC. This area is equal to $DBAE - DBCE$

$$=\{\Sigma n(E_A - E_B) - \Sigma 520n(S_A - S_B)\},$$

where E and S represent the internal energy and entropy values and n is the number of mols of O_2 and N_2 in the air.

The values of S_A and S_B are found as follows. At A the pressure of

The area $BCED = 520(S_A - S_B)$

$$= 520(0{\cdot}02159 - 0{\cdot}01758)$$
$$= 2{\cdot}085 \text{ B.Th.U.}$$

The change of internal energy $(E_A - E_B)$ between A and B is given by

$$n_{O_2}(E_A - E_B)_{O_2} + n_{N_2}(E_A - E_B)_{N_2}.$$
$$= 0{\cdot}0000719(24887 - 2574) + 0{\cdot}0002707(23423 - 2581)$$
$$= 7{\cdot}246 \text{ B.Th.U.}$$

The available energy is thus

$$7{\cdot}246 - 2{\cdot}085$$
$$= 5{\cdot}161 \text{ B.Th.U.}$$

EXAMPLE 5

Calculation of maximum attainable temperature neglecting the formation of NO and assuming no dissociation of N_2 when CO is burned adiabatically at constant volume with the theoretical minimum air supply.

For this combustion, if carried to completion, the reaction equation is

$$CO + \tfrac{1}{2}O_2 + 1{\cdot}881N_2 = CO_2 + 1{\cdot}881N_2,$$

assuming that the air consists of 21 per cent. of O_2 and 79 per cent. of N_2 by volume. Let the initial pressure, volume and temperature of the precombustion mixture be P_1, V_1 and T_1 and the final corresponding values of the dissociated post-combustion mixture be P_2, V_2 and T_2 with $V_2 = V_1$. Let the fractional volume of CO_2 dissociated be x mols per mol of CO_2 so that the amount of CO_2 remaining is $(1-x)$ mols. The oxygen liberated by the dissociation is $\tfrac{1}{2}x$ mols while the CO liberated is x mols. We thus have for the initial and final mixtures:

Initially at P_1, V_1 and T_1		Finally at P_2, V_2 and T_2	
CO	1 mol	CO	x mol
O_2	$\tfrac{1}{2}$ mol	CO_2	$(1-x)$ mol
N_2	1·881 mol	O_2	$\tfrac{1}{2}x$ mol
		N_2	1·881 mol
	Total = 3·381 mol $= m_1$		Total = $(2{\cdot}881 + \tfrac{1}{2}x)$ mol $= m_2$.

Let the partial pressures of the gases CO, CO_2, O_2 and N_2 in the products of combustion be denoted by p_{CO}, p_{CO_2}, p_{O_2} and p_{N_2}. The ratio of these partial pressures of each gas to the total pressure P_2 of the mixture is the same as the ratio of the number of mols of

Since Kp_{CO} is a function of T_2 there are two unknowns involved, namely T_2 and x. Another equation must therefore be established before these can be determined. This is given by the thermal energy equation which is established as follows.

The initial mixture of CO, O_2 and N_2 is considered as being heated at constant volume from T_1 to T_2 without change in composition. The heat required for this is the change in internal energy between T_1 and T_2, that is,

$$(E_{CO}+\tfrac{1}{2}E_{O_2}+1{\cdot}881E_{N_2})_{T_2}-(E_{CO}+\tfrac{1}{2}E_{O_2}+1{\cdot}881E_{N_2})_{T_1}.$$

The CO is now allowed to burn at T_2 to CO_2, liberating the heat of combustion H_{r_2}. The x mols of CO_2 are now dissociated for which the heat required is xH_{r_2}. If the complete process is adiabatic we have,

$$H_{r_2}-xH_{r_2}=(E_{CO}+\tfrac{1}{2}E_{O_2}+1{\cdot}881E_{N_2})_{T_2}-(E_{CO}+\tfrac{1}{2}E_{O_2}+1{\cdot}881E_{N_2})_{T_1}. \quad \ldots(2)$$

An alternative way of regarding the process is as follows. The mol of CO is first burned completely to CO_2 at T_1 so that the heat liberated is H_{r_1}. The products now consist of 1 mol of CO_2 and 1·881 mol of N_2. If these products are heated at constant volume to T_2 they absorb the heat

$$(E_{CO_2}+1{\cdot}881E_{N_2})_{T_2}-(E_{CO_2}+1{\cdot}881E_{N_2})_{T_1},$$

and finally, for the dissociation of x mols of CO_2, the heat required is xH_{r_2}. For adiabatic conditions therefore

$$H_{r_1}-xH_{r_2}=(E_{CO_2}+1{\cdot}881E_{N_2})_{T_2}-(E_{CO_2}+1{\cdot}881E_{N_2})_{T_1}. \quad \ldots\ldots\ldots(3)$$

This can be reduced to equation (2) but it is simpler to use it as it stands in solving for x with assumed T_2 values.

The above equations are now applied to the following particular case. One mol of CO along with the necessary air for theoretically correct combustion is contained in a closed space at a temperature of 600° F. abs. and pressure of 1 atmosphere. It is required to find the maximum attainable temperature due to adiabatic combustion of the CO at constant volume.

From the energy equation (3) we have with $H_{r_1}=121198$ B.Th.U./lb. mol and

$$(E_{CO_2}+1{\cdot}881E_{N_2})_{600}=(3434+1{\cdot}881\times 2979)$$
$$=9037 \text{ B.Th.U./lb. mol.}$$

Hence $$121198-xH_{r_2}=(E_{CO_2}+1{\cdot}881E_{N_2})_{T_2}-9037,$$

or $$xH_{r_2}=130235-(E_{CO_2}+1{\cdot}881E_{N_2})_{T_2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

By assuming values of T_2 the corresponding values of E_{CO_2} and E_{N_2} are found from the tables and x is then calculable from equation (4). Using these calculated values of x, the values of K_p are determined from equation (1) and plotted to a base of T_2 values. The true K_p values, as given by the tables, are also plotted to the same base. The point of intersection of the two curves gives the required upper temperature limit T_2.

The work is conveniently arranged in tabular form as follows :

T_2	$=4800$	4900	5000
E_{CO_2}	$=51606$	52900	54197
$1{\cdot}881E_{N_2}$	$=54229$	55510	56793
$E_{CO_2}+1{\cdot}881E_{N_2}$	$=105835$	108410	110990
	130235	130235	130235
xH_{v_2}	$=24400$	21825	19245
H_{v_2}	$=113050$	112813	112574
x	$=0{\cdot}2158$	$0{\cdot}1935$	$0{\cdot}1710$

At 4800° F. abs.

$$K_p=\frac{(1-x)}{x^{\frac{3}{2}}}\left(\frac{6{\cdot}762\times600}{1\times4800}\right)^{\frac{1}{2}}$$

$$=\frac{0{\cdot}7842}{0{\cdot}2158^{\frac{3}{2}}}\left(\frac{4057{\cdot}2}{4800}\right)^{\frac{1}{2}}$$

$$=7{\cdot}191$$

At 4900° F. abs.

$$K_p=\frac{0{\cdot}8065}{0{\cdot}1935^{\frac{3}{2}}}\left(\frac{6{\cdot}762\times600}{1\times4900}\right)^{\frac{1}{2}}$$

$$=8{\cdot}624.$$

At 5000° F. abs.

$$K_p=\frac{0{\cdot}8290}{0{\cdot}1710^{\frac{3}{2}}}\left(\frac{6{\cdot}762\times600}{1\times5000}\right)^{\frac{1}{2}}$$

$$=10{\cdot}565.$$

The curve AB (fig. 15) represents the true K_p values, while the curve CD represents the curve given by the K_p values calculated above.

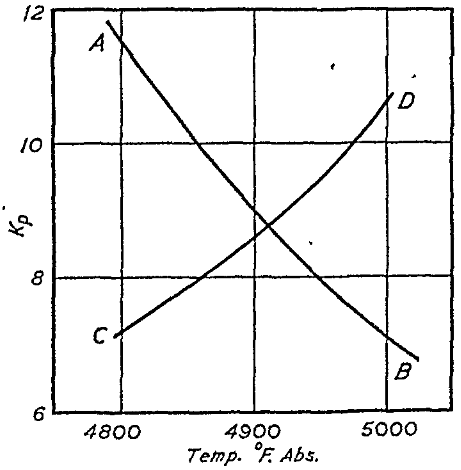

Fig. 15.

The curves intersect at $T_2=4908°$ F. abs. which is therefore the maximum attainable temperature. The corresponding value of x, that

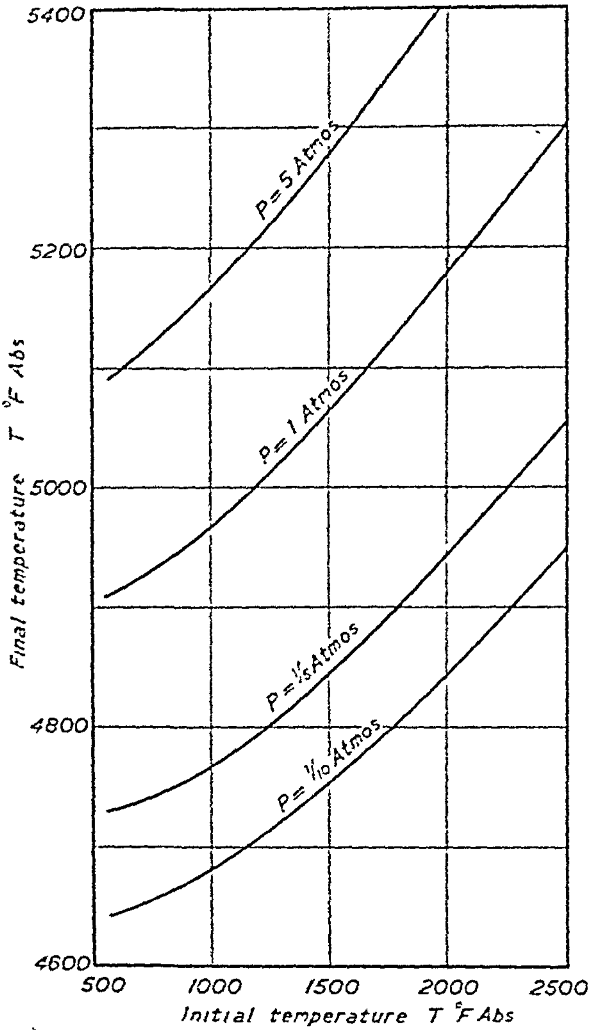

FIG. 16.

is the fractional amount of CO_2 dissociated, can now be found from the tabular calculation of equation (1) as follows :

T_2	= 4908
E_{CO_2}	= 53004
$1{\cdot}881E_{N_2}$	= 55613
$E_{CO_2} + 1{\cdot}881E_{N_2}$	= 108617
	130235
xH_{r_2}	= 21618
H_{r_2}	112832
x	0·1916

The percentage of CO_2 dissociated is thus 19·16.

The curves in fig. 16 show how the maximum attainable temperatures vary with different initial temperatures and different initial pressures, while those in fig. 17 show the percentage dissociation of CO_2. The

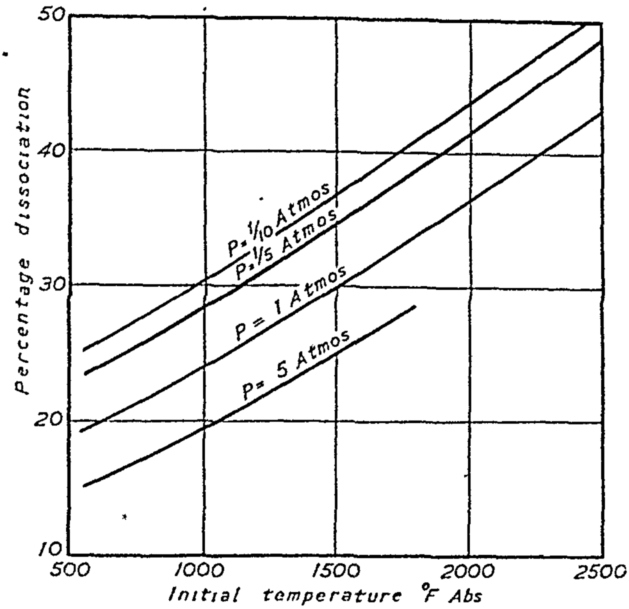

FIG. 17.

points required to plot these curves were obtained in the same way as shown in the sample calculation above, where the initial temperature was 600° F. abs. and the initial pressure was 1 atmosphere.

EXAMPLE 6

Calculation of Maximum Temperature in Gas Engine Cycle

The following data were obtained from a test carried out on a Crossley four-stroke gas engine in the James Watt Engineering Laboratories, The University of Glasgow.

Speed, 218 r.p.m.
Explosions, 100·5 per. min.
Temperature of exhaust gases, 1423° F. abs.
Gas consumption, 3·316 ft.^{3}/min. at S.T.P.
Barometer, 29·37″ Hg. or 14·42 lb./in.^{2} abs.
Air consumption, 1·754 lb./min.
Stroke volume, 0·334 ft.^{3}
Clearance volume, 0·092 ft.^{3}
Pressure at beginning of suction stroke, 14·42 lb./in.^{2} abs.
Pressure at end of suction stroke, 12·98 lb./in.^{2} abs.
Also, assumed composition of air by volume: 79·1% N_2, 20·9% O_2,
and by weight: 76·8% N_2, 23·2% O_2.

Molecular weight of air, 28·84.

From the above it is seen that the volume of air used per minute is

$$1{\cdot}754 \times 359/28{\cdot}84 = 21{\cdot}83 \text{ ft.}^3 \text{ at S.T.P.}$$

Volume of air used per cycle is

$$21{\cdot}83/109 = 0{\cdot}2003 \text{ ft.}^3 \text{ at S.T.P.}$$

Volume of gas used per cycle is

$$3{\cdot}316/100{\cdot}5 = 0{\cdot}0330 \text{ ft.}^3 \text{ at S.T.P.}$$

Air-gas ratio $= 0{\cdot}2003/0{\cdot}0330 = 6{\cdot}070$.

Volume of nitrogen in air supply per ft.^{3} of fuel gas is

$$0{\cdot}791 \times 6{\cdot}070 = 4{\cdot}8014 \text{ ft.}^3$$

Volume of oxygen in air supply per ft.^{3} of fuel gas is

$$0{\cdot}209 \times 6{\cdot}070 = 1{\cdot}2686 \text{ ft.}^3$$

For the determination of the ideal maximum gas temperature from the data found by experiment the following method has been adopted. The fuel gas analysis and air gas ratio enable the analysis of the post-combustion mixture to be obtained and this is assumed to be the same as that of the gases filling the clearance volume at the beginning of the suction stroke. Also the measured temperature of the gases leaving the engine is assumed to be the same as that of the gases filling the clearance volume at the beginning of suction so that the weight of these gases can be determined. The sum of the weights of the air, gas and residuals gives the total weight of the charge at the beginning of compression. The gas constant of the charge is found by calculation and hence the temperature at the beginning of compression can be determined.

The temperature T_2 at the end of isentropic compression is found by trial and error as follows. A tentative value of T_2 is first assumed and from this the absolute entropy of the charge is calculated. If this is found to be the same as the absolute entropy of the charge at the beginning of compression, i.e. at T_1, the assumed value of T_2 is correct; otherwise a new value of T_2 is again assumed and the procedure is continued until the stated condition is satisfied.

In order to find T_3, the temperature at the end of constant volume burning, the following method is adopted. From the calculated volumetric analysis of the charge the composition of the products with no dissociation is first determined and from this the composition of the products with dissociation is expressed in terms of x, y, u, and z, where

x = the number of mols of CO_2 dissociated to CO and O_2
y = the number of mols of H_2O dissociated to H_2 and O_2
u = the number of mols of H_2O dissociated to H_2 and OH.
z = the number of mols of NO formed from O_2 and N_2.

The attainment of the final state of the constant volume burning period can be imagined as occurring in the following steps. The charge is

first burned isothermally and completely, i.e. without dissociation, at T_2, the temperature at the end of compression. The products thus formed are then heated to an assumed equilibrium temperature T_3 after which they are dissociated, at this temperature, to give the final equilibrium state. The heat liberated by the combustion of the charge at T_2 must, under adiabatic conditions, be equal to that required to heat the products from T_2 to T_3 together with that required to effect the dissociation. An equation connecting x, y, u and z can thus be established. Since, however, there are five unknowns, namely, T_3, x, y, u and z, four other equations are required for a complete solution. These are supplied by the equilibrium constants $(K_p)_{w.g.}$, $(K_p)_{CO_2}$, $(K_p)_{OH}$ and $(K_p)_{NO}$. If the five equations are satisfied the assumed value of T_3 is correct, otherwise further trial and error is required until the conditions are satisfied.

The analysis of the Glasgow Corporation gas used in the test was as follows:

Gas	v	m	mv	w fractional
CO_2	0·033	44	1·452	0·1079
C_nH_m (assumed C_2H_4)	0·020	28	0·560	0·0416
O_2	0·009	32	0·288	0·0214
CO	0·152	28	4·256	0·3163
CH_4	0·180	16	2·880	0·2140
H_2	0·498	2	0·996	0·0740
N_2	0·108	28	3·024	0·2248
Apparent molecular weight, $\Sigma mv = 13{\cdot}456$				1·0000

From this analysis of the fuel gas and the air gas ratio of 6·070, found above, the composition of the post-combustion mixture can now be found. This composition is assumed to be the same as that of the products which fill the clearance volume at the beginning of the suction stroke.

In fuel gas	Vol.	Vol. of CO_2 formed	Vol. of H_2O formed	Vol. of O_2 required
C_2H_4	0·020	0·040	0·040	0·060
CO	0·152	0·152	—	0·076
CH_4	0·180	0·180	0·360	0·360
H_2	0·498	—	0·498	0·249
CO_2	0·033	0·033	—	—
O_2	0·009	—	—	0·009
N_2	0·108	—	—	—
		$\Sigma CO_2 = 0{\cdot}405$	$\Sigma H_2O = 0{\cdot}898$	$\Sigma O_2 = 0{\cdot}736$

The excess volume of oxygen in the products is

$$1{\cdot}2686-0{\cdot}7360=0{\cdot}5326 \text{ ft.}^3$$

and the volume of nitrogen in the products is

$$4{\cdot}8014+0{\cdot}1080=4{\cdot}9094 \text{ ft.}^3$$

The apparent molecular weight of the products is found tabularly as follows:

Gas	v per ft.³ of gas	v fractional	m	mv
CO_2	0·4050	0·0600	44	2·640
H_2O	0·8980	0·1331	18	2·396
O_2	0·5326	0·0790	32	2·528
N_2	4·9094	0·7279	28	20·381
	6·745	1·0000	$\Sigma mv=27{\cdot}945$	

The apparent molecular weight $=\dfrac{\Sigma mv}{v}=\dfrac{27{\cdot}945}{1}=27{\cdot}95$ say. The universal gas constant $=1546$ (with $R/J=1{\cdot}9869$). Hence the gas constant for the products is $1546/27{\cdot}95=55{\cdot}31\ \dfrac{\text{ft. lb.}}{\text{lb.}\times{}^\circ\text{F.}}$ and the weight of the residuals is given by

$$w_r=\frac{144\times 14{\cdot}42\times 0{\cdot}092}{55{\cdot}31\times 1423}=0{\cdot}002427 \text{ lb.}$$

The gas constant for the gaseous fuel is

$$R_g=1546/13{\cdot}46=114{\cdot}9\ \frac{\text{ft. lb.}}{\text{lb.}\times{}^\circ\text{F.}}$$

so that the density of the gaseous fuel is

$$\rho_g=144\times 14{\cdot}696/114{\cdot}9\times 492=0{\cdot}0374 \text{ lb./ft.}^3 \text{ at S.T.P.}$$

The weight of gas supplied per working cycle is

$$w_g=v_g\rho_g$$

or

$$w_g=\frac{V_g\rho_g}{n}$$

where V_g is the volume of gas used per minute and n is the number of explosions per minute.

This gives

$$w_g=3{\cdot}316\times 0{\cdot}0374/100{\cdot}5=0{\cdot}001234 \text{ lb.}$$

The weight of air used per cycle is

$$w_a=\frac{W_a}{N/2}=1{\cdot}754/109=0{\cdot}016092 \text{ lb.}$$

where W_a is the weight of air supplied per minute and N is the speed in revolutions per minute.

The total weight of the charge is thus

$$W = w_r + w_a + w_g$$
$$= 0{\cdot}002427 + 0{\cdot}016092 + 0{\cdot}001234$$
$$= 0{\cdot}019753 \text{ lb.}$$

The gas constant for the charge is given by

$$R = \frac{w_r R_r + w_g R_g + w_a R_a}{W}$$
$$= \frac{0{\cdot}002427 \times 53{\cdot}31 + 0{\cdot}001234 \times 114{\cdot}9 + 0{\cdot}016092 \times 53{\cdot}58}{0{\cdot}019753}$$
$$= 57{\cdot}62 \ \frac{\text{ft. lb.}}{\text{lb.} \times {}^\circ \text{F.}}$$

The temperature at the beginning of compression is given by

$$T_1 = \frac{144 \times 12{\cdot}98 \times 0{\cdot}426}{0{\cdot}019753 \times 57{\cdot}62}$$
$$= 699{\cdot}5 \text{ or say}$$
$$700^\circ \text{ F. abs.}$$

The volume of the residuals at 14·42 lb./in.^{2} abs. and 1423° F. abs. is 0·092 ft.^{3} so that the volume under S.T.P. conditions is

$$v_r' = \frac{0{\cdot}092 \times 492 \times 14{\cdot}42}{14{\cdot}696 \times 1423}$$
$$= 0{\cdot}0312 \text{ ft.}^3$$

The S.T.P. volume of fuel gas used per cycle is 0·0330 ft.^{3} (page 45) so that the volume of residuals per ft.^{3} of fuel gas is

$$0{\cdot}0312/0{\cdot}0330 = 0{\cdot}9454 \text{ ft.}^3$$

The composition of the residuals is given on page 47 so that the volume of CO_2, H_2O, O_2 and N_2 in the residuals per ft.^{3} of fuel gas is found by multiplying each of the respective fractional volumes by 0·9454. This gives

CO_2	$0{\cdot}0600 \times 0{\cdot}9454 = 0{\cdot}0567$
H_2O	$0{\cdot}1331 \times 0{\cdot}9454 = 0{\cdot}1258$
O_2	$0{\cdot}0790 \times 0{\cdot}9454 = 0{\cdot}0747$
N_2	$0{\cdot}7279 \times 0{\cdot}9454 = 0{\cdot}6882$

Adding these to the total air and constituents of fuel gas the composition of the charge is as shown below:

	C_2H_4	CO	CH_4	H_2	CO_2	H_2O	O_2	N_2
Residuals	—	—	—	—	0·0567	0·1258	0·0747	0·6882
Air	—	—	—	—	—	—	1·2686	4·8014
Fuel gas	0·0200	0·1520	0·1800	0·4980	0·0330	—	0·0090	0·1080
Total	0·0200	0·1520	0·1800	0·4980	0·0897	0·1258	1·3523	5·5976
No. of mols per mol of charge	0·00250	0·01896	0·02246	0·06213	0·01119	0·01569	0·16871	0·69836

Pressure and Temperature of Charge at end of Compression

The composition of the charge given above enables the absolute entropy (S_1) to be determined at the beginning of compression and this must equal the absolute entropy (S_2) of the charge at the end of isentropic compression. Following the procedure indicated in example 2 we have (see equation 3, p. 30)

$$S_1 - S_2 = 0 = \Sigma m(S_T)_1 + \frac{R}{J}\log_e\frac{r_c}{T_1} - \Sigma m(S_T)_2 + \frac{R}{J}\log_e T_2 \quad \ldots\ldots(1)$$

where r_c is the compression ratio. The first two terms on the right-hand side of the equation have a constant value and are therefore determined before proceeding with the subsequent trial and error calculation. Arranging the work in tabular form gives (with $T_1 = 700°$ F. abs.)

	$m(S_T)_1$
(for C_2H_4)	$0{\cdot}00250 \times 56{\cdot}466 = 0{\cdot}14117$
(for CO)	$0{\cdot}01896 \times 49{\cdot}182 = 0{\cdot}93249$
(for CH_4)	$0{\cdot}02246 \times 46{\cdot}826 = 1{\cdot}05171$
(for H_2)	$0{\cdot}06213 \times 33{\cdot}078 = 2{\cdot}05513$
(for CO_2)	$0{\cdot}01119 \times 53{\cdot}569 = 0{\cdot}59944$
(for H_2O)	$0{\cdot}01569 \times 47{\cdot}285 = 0{\cdot}74137$
(for O_2)	$0{\cdot}16871 \times 50{\cdot}913 = 8{\cdot}58953$
(for N_2)	$0{\cdot}69836 \times 47{\cdot}648 = 33{\cdot}27546$
	$\Sigma m(S_T)_1 \quad 47{\cdot}38630$

The second term in equation (1) is

$$\frac{R}{J}\log_e\frac{r_c}{T_1} = -1{\cdot}9869 \times 2{\cdot}303 \log\frac{700}{4{\cdot}631}$$
$$= -9{\cdot}97088$$

From previous trial and error methods it is found that with $T_2 = 1235°$ F. abs. equation (1) is satisfied. This is confirmed as follows. The value of the last term in equation (1) is now given by

$$\frac{R}{J}\log_e T_2 = 1{\cdot}9869 \times 2{\cdot}30258 \log 1235$$
$$= 14{\cdot}1444.$$

The value of $m(S_T)_2$ is conveniently found tabularly as follows:

	$m(S_T)_2$
(for C_2H_4)	$0{\cdot}00250 \times 65{\cdot}697 = 0{\cdot}16424$
(for CO)	$0{\cdot}01896 \times 53{\cdot}240 = 1{\cdot}00943$
(for CH_4)	$0{\cdot}02246 \times 53{\cdot}267 = 1{\cdot}19638$
(for H_2)	$0{\cdot}06213 \times 37{\cdot}039 = 2{\cdot}30123$
(for CO_2)	$0{\cdot}01119 \times 59{\cdot}687 = 0{\cdot}66790$
(for H_2O)	$0{\cdot}01569 \times 52{\cdot}098 = 0{\cdot}81742$
(for O_2)	$0{\cdot}16871 \times 55{\cdot}156 = 9{\cdot}30537$
(for N_2)	$0{\cdot}69836 \times 51{\cdot}680 = 36{\cdot}09124$
	$51{\cdot}55321$

These calculated values, when inserted in equation (1), give

$$S_1 - S_2 = 47{\cdot}38630 - 9{\cdot}97088 - 51{\cdot}5532 + 14{\cdot}1444$$
$$= 0{\cdot}00661 \text{ E.U.}$$

which is near enough zero to justify the assumed value of 1235° F. abs. for T_2. The corresponding pressure is found from

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

or

$$p_2 = \frac{p_1V_1T_2}{V_2T_1}$$
$$= \frac{12{\cdot}98 \times 4{\cdot}631 \times 1235}{1 \times 700}$$
$$= 106{\cdot}1 \text{ lb./in.}^2 \text{ abs.}$$
or 7·220 atmospheres.

The composition of the charge is given on page 48, but the composition of the products formed with complete combustion is required. This is conveniently found from the following table.

	Mols produced		Mols of O_2 required	N_2
	CO_2	H_2O		
Combustion of—				
0·00250 mols of C_2H_4	0·00500	0·00500	0·00750	
0·01896 mols of CO	0·01896	—	0·00948	
0·02246 mols of CH_4	0·02246	0·04492	0·04492	
0·06213 mols of H_2	—	0·06213	0·03107	
Total	0·04642	0·11205	0·09297	
CO_2 present in charge	0·01119			
H_2O present in charge		0·01569		
O_2 present in charge			0·16871	
N_2 present in charge				0·69836
Total in products	0·05761	0·12774	0·07574	0·69836

The composition of the products with complete combustion is thus

$$\left.\begin{array}{ll} CO_2 & 0{\cdot}05761 \\ H_2O & 0{\cdot}12774 \\ O_2 & 0{\cdot}07574 \\ N_2 & 0{\cdot}69836 \end{array}\right\} \text{per mol of charge.}$$
$$\underline{\underline{0{\cdot}95945}}$$

Constant Volume Burning

Proceeding now along the lines indicated on p. 45 the heat of combustion of one mol of the charge at $T_2 = 1235°$ F. abs. and at constant volume, is first required. This is given by

$$H_v = \Sigma m H_v$$
$$= 0{\cdot}00250 \times 569916 + 0{\cdot}01896 \times 120714 + 0{\cdot}02246 \times 343952 + 0{\cdot}06213 \times 104359$$
$$= 17922{\cdot}4 \text{ B.Th.U./lb. mol.}$$

The products, the analysis of which is given on p. 50, are now heated at constant volume from $T_2 = 1235°$ F. abs. to the unknown final temperature T_3 which has at first to be assumed tentatively. The heat required for this is

$$\Sigma m(E_{T_3} - E_{1235})$$
$$= [0{\cdot}05761E_{CO_2} + 0{\cdot}12774E_{H_2O} + 0{\cdot}07574E_{O_2} + 0{\cdot}69836E_{N_2}]_{T_3}$$
$$- 0{\cdot}05761 \times 8941 - 0{\cdot}12774 \times 7733 - 0{\cdot}07574 \times 6453 - 0{\cdot}69836 \times 6234$$
$$= [0{\cdot}05761E_{CO_2} + 0{\cdot}12774E_{H_2O} + 0{\cdot}07574E_{O_2} + 0{\cdot}69836E_{N_2}]_{T_3} - 6345.$$

If the products are now dissociated the heat required is

$$[xH_{vCO} + yH_{vH_2} + uH_{vOH} + zH_{vNO}]_{T_3}.$$

We thus have

$$17922 = [0{\cdot}05761E_{CO_2} + 0{\cdot}12774E_{H_2O} + 0{\cdot}07574E_{O_2} + 0{\cdot}69836E_{N_2}]_{T_3} - 6345 + [xH_{vCO} + yH_{vH_2} + uH_{vOH} + zH_{vNO}]_{T_3}.$$

This gives

$$[xH_{vCO} + yH_{vH_2} + uH_{vOH} + zH_{vNO}]_{T_3}$$
$$= 24267 - [0{\cdot}05761E_{CO_2} + 0{\cdot}12774E_{H_2O} + 0{\cdot}07574E_{O_2} + 0{\cdot}69836E_{N_2}]_{T_3} \quad (1)$$

From several trials it has been found that equation (1) along with the equilibrium constants is satisfied when $T_3 = 3872°$ F. abs. (T_3 is found by the method explained on p. 45.) This is confirmed as follows.

At $T_3 = 3872°$ F. abs. equation (1) becomes

$$24267 - [115236x + 104378y + 121041u + 38827z]$$
$$= 24267 - [0{\cdot}05761 \times 39747 + 0{\cdot}12774 \times 31376 + 0{\cdot}07574 \times 23974 + 0{\cdot}69836 \times 22567]$$
$$= 24267 - 23889$$
$$= 393,$$

which gives

$$z = 0{\cdot}010122 - 2{\cdot}967934x - 2{\cdot}688284y - 3{\cdot}117444u. \quad \text{.........(2)}$$

As explained on p. 45, x denotes the number of mols of CO_2 dissociated in accordance with the reaction equation

$$xCO + \tfrac{1}{2}xO_2 = xCO_2.$$

Hence the numbers of mols of CO and O_2 formed, due to this reaction, are x and $\frac{1}{2}x$ respectively while the number of mols of CO_2 is reduced

by x, giving $(0{\cdot}05761 - x)$ mols. Similarly, due to the dissociation of y mols of H_2O in accordance with the reaction equation

$$yH_2 + \tfrac{1}{2}yO_2 = yH_2O,$$

we have y mols of H_2 and $\frac{1}{2}y$ mols of O_2 formed, leaving $(0{\cdot}12774 - y)$ mols of H_2O. Due to the dissociation of u mols of H_2O in accordance with the reaction equation

$$\tfrac{1}{2}uH_2 + uOH = uH_2O,$$

we have $\frac{1}{2}u$ mols of H_2 and u mols of OH formed, leaving $(0{\cdot}12774 - y - u)$ mols of H_2O. Finally, due to the formation of z mols of NO in accordance with the reaction equation

$$zNO = \tfrac{1}{2}zN_2 + \tfrac{1}{2}zO_2,$$

we have z mols of NO formed while the N_2 and O_2 are each reduced by $\frac{1}{2}z$ mols.

The composition of the post-combustion dissociated mixture at P_3, V_3 and T_3 is thus as follows :

Gas	No. of mols
CO	x
CO_2	$0{\cdot}05761 - x$
H_2O	$0{\cdot}12774 - u - y$
H_2	$y + 0{\cdot}5u$
OH	u
O_2	$0{\cdot}07574 + 0{\cdot}5x + 0{\cdot}5y - 0{\cdot}5z$
NO	z
N_2	$0{\cdot}69836 - 0{\cdot}5z.$

Total mols $= m_3 = 0{\cdot}959$[illegible]$+ 0{\cdot}5x + 0{\cdot}5y + 0{\cdot}5u.$

The number of mols in the precombustion mixture is $m_2 = 1$.

The partial pressures of the gases in the dissociated state are expressed by the following relationships :

$$\frac{p_{CO_2}}{P_3} = \frac{0{\cdot}05761 - x}{m_3},$$

but $\qquad P_2V_2 = m_2RT_2$

and $\qquad P_3V_3 = m_3RT_3,$

so that

$$\frac{P_2}{P_3} = \frac{m_2T_2}{m_3T_3},$$

or

$$\frac{P_3}{m_3} = \frac{P_2T_3}{m_2T_2}.$$

Hence,

$$p_{CO_2} = (0{\cdot}05761 - x)\,\frac{P_2T_3}{m_2T_2}.$$

Similarly,

$$p_{CO}=\frac{P_2T_3x}{m_2T_2},$$

$$p_{H_2O}=\frac{(0{\cdot}12774-u-y)P_2T_3}{m_2T_2},$$

$$p_{H_2}=\frac{(y+0{\cdot}5u)P_2T_3}{m_2T_2},$$

$$p_{OH}=\frac{P_2T_3u}{m_2T_2},$$

$$p_{O_2}=\frac{(0{\cdot}07574+0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)P_2T_3}{m_2T_2},$$

$$p_{NO}=\frac{P_2T_3z}{m_2T_2},$$

$$p_{N_2}=\frac{(0{\cdot}69836-0{\cdot}5z)P_2T_3}{m_2T_2}.$$

The equilibrium constants are given by the following expressions:

$$K_{pCO_2}=\frac{p_{CO_2}}{p_{CO}\cdot p_{O_2}^{\frac{1}{2}}}$$

$$=\frac{(0{\cdot}05761-x)}{x(0{\cdot}07574+0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}}\left(\frac{m_2T_2}{P_2T_3}\right)^{\frac{1}{2}},$$

but $m_2=1$; $T_2=1235°$ F. abs.; $P_2=7{\cdot}220$ atm., giving

$$K_{pCO_2}=\frac{13{\cdot}079(0{\cdot}05761-x)}{x(0{\cdot}07574+0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}\,T_3^{\frac{1}{2}}} \quad \text{.....(3)}$$

$$K_{p\,w.g.}=\frac{p_{CO}\cdot p_{H_2O}}{p_{H_2}\cdot p_{CO_2}}$$

$$=\frac{x(0{\cdot}12774-u-y)}{(0{\cdot}05761-x)(y+0{\cdot}5u)} \quad \text{.....(4)}$$

$$K_{pOH}=\frac{p_{H_2O}}{p_{OH}\cdot p_{H_2}^{\frac{1}{2}}}$$

$$=\frac{13{\cdot}079(0{\cdot}12774-u-y)}{u(y+0{\cdot}5u)^{\frac{1}{2}}\,T_3^{\frac{1}{2}}} \quad \text{.....(5)}$$

$$K_{pNO}=\frac{p_{NO}}{p_{N_2}^{\frac{1}{2}}\,p_{O_2}^{\frac{1}{2}}}$$

$$=\frac{z}{(0{\cdot}69836-0{\cdot}5z)^{\frac{1}{2}}(0{\cdot}07574+0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \text{.....(6)}$$

Equations (2), (3), (4), (5) and (6) form the conditions of equilibrium and the method of solution is as follows. A probable value of T_3 is first guessed and, with $y=0$, u is determined from equation (5). Substituting these values for u and y in equation (4) the value of x is determined.

Equation (2) can then be solved to give the value of z. Equation (3) must now be satisfied by the values of x, y and z as obtained above. If equation (3) is not satisfied another value for y must be assumed and the process repeated until equation (3) is satisfied. If these assumed values are correct equation (6) must also be satisfied. If not, the whole process is repeated with a new value for T_3 until all equations are satisfied simultaneously.

Solving the equations in the above manner gave $T_3 = 3872°$ F. abs. with $u = 0{\cdot}001450$ and $y = -0{\cdot}0006434$ as shown by equation (5). Thus with $K_{p_{OH}} = 2036$ at $T_3 = 3872°$ F. abs. we have, for the right-hand side of equation (5),

$$\frac{13{\cdot}079\,(0{\cdot}12774 - 0{\cdot}001450 + 0{\cdot}0006434)}{0{\cdot}002565\,(0{\cdot}000737 - 0{\cdot}0006545)^{\frac{1}{2}} \times 62{\cdot}225}$$
$$= 2037,$$

so that the equation is satisfied.

Substituting these values in equation (4) gives

$$x = 0{\cdot}00019594\,; \quad (K_{p_{w.g.}})_{T_3=3874} = 5{\cdot}3088.$$

Equation (2) now gives

$$z = 0{\cdot}006750.$$

If the assumed values of T_3 and u are correct, it will be found that the derived values of x, y and z satisfy equations (3) and (6).

Thus the right-hand side of equation (3) is 229·5 as against 227 given in the tables for $K_{p_{CO_2}}$ and the right-hand side of equation (6) is 0·03015 as against 0·02961 given in the tables for $K_{p_{NO}}$.

Hence the maximum attainable temperature is 3872° F. abs.

Chemical Reaction

$$CO + \tfrac{1}{2}O_2 + 1{\cdot}881N_2 \rightarrow CO_2 + 1{\cdot}881N_2.$$

This gives, as the working substance, 1 mol of $CO_2 + 1{\cdot}881$ mols of N_2 and it will be assumed that this mixture completely fills the cylinder at the beginning of compression, the pressure being one atmosphere and the temperature 600° F. abs.

Compression

$$P_1 = 1\ ;\ V_1 = 5\ ;\ T_1 = 600° \text{ F. abs.}$$

The total entropy for a mixture of gases at any pressure P and temperature T is given by

$$S = \Sigma(mS_T) + \Sigma m \frac{R}{J} \log_e \frac{\Sigma m}{m} - \Sigma m \frac{R}{J} \log_e P.$$

Hence at the beginning of compression the entropy, as shown in the following table, is 143·405.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4{\cdot}575m \log_{10} \frac{\Sigma m}{m}$
CO_2	1	52·104	52·104	2·8810	0·45954	2·102
N_2	1·881	46·574	87·606	1·5316	0·18514	1·593
	$\Sigma m = 2{\cdot}881$;		$\Sigma(mS_T) = 139{\cdot}710$;			$\Sigma\left(4{\cdot}575m \log_{10} \frac{\Sigma m}{m}\right) = 3{\cdot}695$

$$S_{600} = 139{\cdot}710 + 3{\cdot}695 = 143{\cdot}405 \text{ E.U.}$$

The pressure and temperature at the end of compression are found to be 8·4301 atmospheres and 1012° F. abs. respectively, the entropy being 143·405 E.U.

Constant Volume Heating

The heat available for heating the CO_2 and N_2 will be taken as the heat of reaction at constant volume of one mol of CO at 1012° F. abs. which according to the tables is 120990 B.Th.U. Using this value for the heat available the maximum temperature attainable in the cylinder may be determined and the amount of dissociation. Denoting the number of mols of CO_2 dissociated by x, the value of K_{pCO_2} at any temperature T_3 is given by

$$K_{pCO_2} = \frac{(1-x)}{x(0{\cdot}5x)^{\frac{1}{2}}} \left(\frac{m_2 T_2}{P_2 T_3}\right)^{\frac{1}{2}},$$

where the suffix 2 refers to conditions at the end of compression. See figure 18.

$$m_2 = 2{\cdot}881\ ;\ T_2 = 1012° \text{ F. abs. and } P_2 = 8{\cdot}4301 \text{ atmospheres,}$$

so that

$$K_{pCO_2} = \frac{18{\cdot}597(1-x)}{x(0{\cdot}5x)^{\frac{1}{2}}} \cdot \frac{1}{T_3^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The second equation required for the determination of T_3 and x is supplied by the energy relationship

$$H_{v_2}=[E_{CO_2}+1\cdot881E_{N_2}]_{T_2}^{T_3}+(x\,H_{v_3})_{CO} \quad\text{.................}(2)$$

where the suffix 3 refers to the point on the diagram at the end of constant volume combustion. T_2 is known so that equation (2) becomes

$$120990=[E_{CO_2}+1\cdot881E_{N_2}]_{T_3}-6832-9518+(xH_{v_3})_{CO}$$

or

$$xH_{v_3}=137340-[E_{CO_2}+1\cdot881E_{N_2}]_{T_3}. \quad\text{.................}(3)$$

By choosing a series of values for T_3 a corresponding set of values of x is found from equation (3) and the correct value of T_3 is obtained when the corresponding value of x satisfies equation (1). This is found to be the case when $T_3=5252°$ F. abs., giving for equation (3)

$$111977x=137340-57473-60034,$$

from which

$$x=0\cdot1771.$$

Substituting $x=0\cdot1771$ in the right-hand side of equation (1) gives

$$K_{p_{CO_2}}=4\cdot0070,$$

which is very close to the tabulated value at 5252° F. abs.

So far the calculation has given the compression line and the temperature attained at the end of constant volume heating, but the shape of the curve representing combustion has still to be determined. If the heating of the CO_2 and N_2 proceeds to completion through a series of equilibrium state points equation (1) must give the relation between x and T at any temperature T. With the composition of the gases fixed at each temperature the entropy may be calculated for the corresponding gaseous mixture and the state points plotted on a temperature-entropy diagram.

The following table gives the values of x for a series of temperatures from 3000° F. abs., below which x is insignificant, to 5252° F. abs., the maximum temperature reached, together with the total entropy at the same temperatures.

T° F. abs.	x	S
3000	0·000808	167·015 (taking $x=0$)
3500	0·0052	171·003
4000	0·0205	174·814
4500	0·0582	178·801
5000	0·1286	183·154
5252	0·1771	185·467

The details of the calculation are shown below for $T_3=5252°$ F. abs.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10}\frac{\Sigma m}{m}$	$4{\cdot}575m\log_{10}\frac{\Sigma m}{m}$
CO	0·17710	65·233	11·553	16·7680	1·22449	0·992
CO_2	0·82290	79·530	65·445	3·6086	0·55732	2·098
O_2	0·08855	67·728	5·997	33·5350	1·52550	0·618
N_2	1·88100	63·546	119·530	1·5787	0·19830	1·706

$\Sigma m = 2{\cdot}96955$; $\Sigma(mS_T) = 202{\cdot}525$; $\Sigma\left(4{\cdot}575m\log_{10}\frac{\Sigma m}{m}\right) = 5{\cdot}414$

$$P_3 = \frac{8{\cdot}4301 \times 2{\cdot}96955 \times 5252}{2{\cdot}881 \times 1012}$$
$$= 45{\cdot}095 \text{ atmospheres.}$$

$$S \text{ at } 5252^\circ \text{ F. abs.} = 202{\cdot}525 + 5{\cdot}414 - 2{\cdot}96955 \times 4{\cdot}575 \log_{10} 45{\cdot}095$$
$$= 185{\cdot}467 \text{ E.U.}$$

The state points between 1012° F. abs. and 3000° F. abs. are the same as those obtained when no dissociation occurs and may be obtained from the table given on page 59. The temperature T_4 at the end of isentropic expansion is given by the point of intersection of the constant volume curve through 1 and the perpendicular through the point 3.

Constant Volume Curve 1–4

The location of points on this curve is similar to that outlined above for the curve 2–3. The equilibrium constant at any temperature T is given by the expression

$$K_{pCO_2} = \frac{(1-x)}{x(0{\cdot}5x)^{\frac{1}{2}}}\left(\frac{m_1 T_1}{P_1 T}\right)^{\frac{1}{2}} \quad \text{.......................(4)}$$

where the suffix 1 refers to the point at the beginning of compression with $m_1 = 2{\cdot}881$, $T_1 = 600^\circ$ F. abs. and $P_1 = 1$ atmosphere.

Substituting these values in equation (4) gives

$$K_{pCO_2} = \frac{41{\cdot}576(1-x)}{x(0{\cdot}5x)^{\frac{1}{2}}\,T^{\frac{1}{2}}} \quad \text{..........................(5)}$$

For any value of T, K_{pCO_2} is fixed so that x can be determined. The total entropy of the mixture is then calculable. The following table gives the values of x for a series of temperatures from 2500° F. abs. where x is taken as zero to 4125° F. abs. where it will be found that the vertical from the point 3 cuts the constant volume curve.

T° F. abs.	x	S.
2500	0	171·851
3000	0·00138	176·285
3500	0·00886	180·344
4000	0·03478	184·477
4125	0·04606	185·571

The calculation for S at 4125° F. abs. is given below and it will

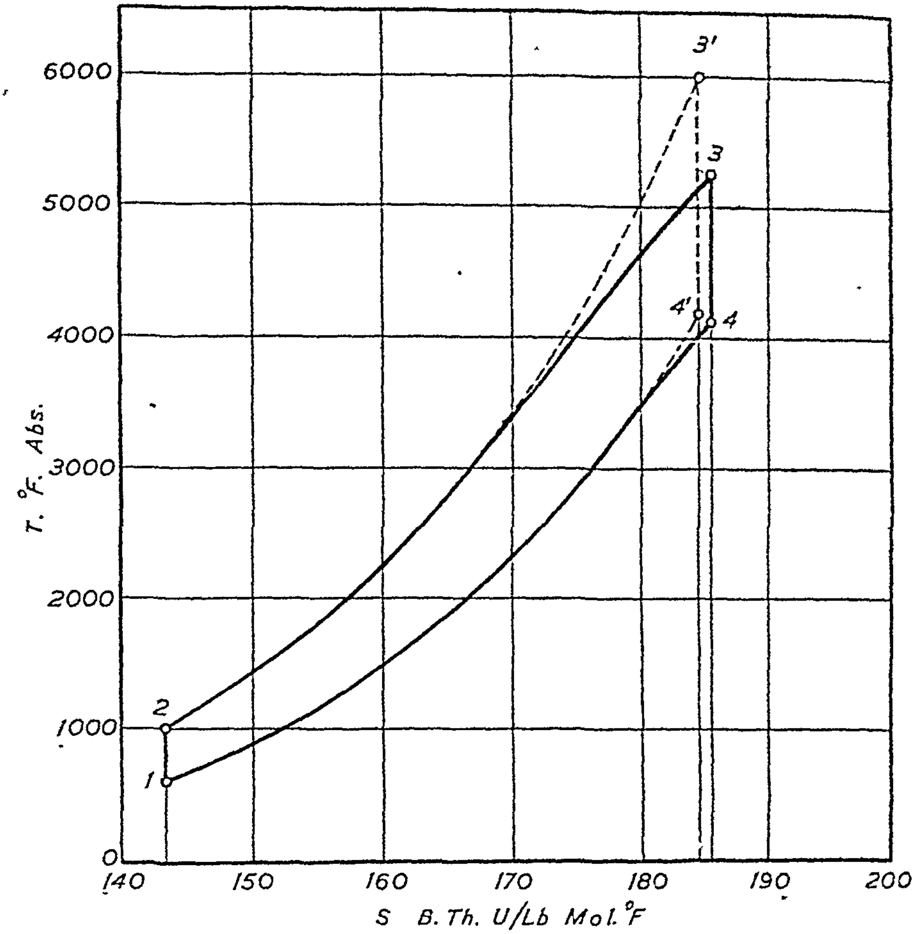

Fig. 18.

be seen that the value obtained is not appreciably different from 185·467 E.U.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10}\frac{\Sigma m}{m}$	$4{\cdot}575m\log_{10}\frac{\Sigma m}{m}$
CO	0·04606	63·102	2·906	63·049	1·79967	0·379
CO_2	0·95394	75·947	72·449	3·0412	0·48347	2·110
O_2	0·02303	65·474	1·508	126·10	2·10071	0·221
N_2	1·88100	61·426	115·542	1·5439	0·18892	1·626

$\Sigma m = 2{\cdot}90403$; $\Sigma mS_T = 192{\cdot}405$; $\Sigma\left(4{\cdot}575m\log_{10}\frac{\Sigma m}{m}\right) = 4{\cdot}336$

$$P_4 = \frac{1 \times 2{\cdot}90403 \times 4125}{2{\cdot}881 \times 600}$$
$$= 6{\cdot}930 \text{ atmos.}$$

$$S \text{ at } 4125° \text{ F. abs.} = 192{\cdot}405 + 4{\cdot}336 - 11{\cdot}170$$
$$= 185{\cdot}571 \text{ E.U.}$$

The state points between 600° F. abs. and 2500° F. abs. inclusive may be obtained from the table on page 60 for the undissociated gas mixture. The cycle, taking into account the dissociation of CO_2 and

neglecting the formation of NO, can now be drawn on the temperature-entropy diagram. To show the effect dissociation has on the cycle it is convenient at this stage to plot the cycle, when dissociation is neglected, on the same diagram as that in which dissociation is taken into account.

Ideal Cycle without Dissociation

Compression. The compression curve is the same as that in the cycle in which dissociation is taken into account.

Heat Reception at Constant Volume

Before calculating the entropies for a series of temperatures the maximum temperature which can be reached should be calculated. The heat available for increasing the internal energy of the CO_2 and N_2 will be the lower heat of reaction at constant volume, H_{r_2}, which, as previously determined, is 120990 B.Th.U./lb. mol. This heat goes to increase the internal energy of the CO_2 and N_2 while satisfying the following thermal relation.

$$120990 = [E_{CO_2} + 1{\cdot}881 E_{N_2}]_{T_2}^{T_3'}. \quad \dots\dots (6)$$

$T_2 = 1012°$ F. abs. and equation (6) becomes

$$120990 = [E_{CO_2} + 1{\cdot}881 E_{N_2}]_{T_3'} - 6832 - 9518$$

or

$$137340 = [E_{CO_2} + 1{\cdot}881 E_{N_2}]_{T_3'}. \quad \dots\dots (7)$$

Equation (7) is approximately solved with $T_3' = 6015°$ F. abs. which gives the right-hand side as $67441 + 69919 = 137360$ as against 137340 for the left-hand side.

Using the general expression for the entropy the following table may be drawn up for the curve of constant volume heating, the pressures in atmospheres being given along with the entropy at temperatures from 2000°F. abs. to 6015° F. abs.

$T°$ F. abs.	P (atmos.)	S
2000	16·660	157·485
2500	20·825	162·638
3000	24·990	167·015
3500	29·155	170·813
4000	33·321	174·170
4500	37·486	177·153
5000	41·651	179·855
5500	45·816	182·323
6015	50·106	184·655

The calculation for the entropy and pressure is given below for 6015° F. abs.

$$P_{3'} = \frac{6015}{1012} \times 8{\cdot}4301 = 50{\cdot}106 \text{ atmospheres.}$$

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4{\cdot}575m \log_{10} \frac{\Sigma m}{m}$
CO_2	1	81·571	81·571	2·8810	0·45954	2·102
N_2	1·881	64·750	121·795	1·5316	0·18514	1·593

$\Sigma m = 2{\cdot}881$; $\Sigma(mS_T) = 203{\cdot}366$; $\Sigma\left(4{\cdot}575m \log_{10} \frac{\Sigma m}{m}\right) = 3{\cdot}695$

S at 6015° F. abs.

$= 203{\cdot}366 + 3{\cdot}695 - 2{\cdot}881 \times 4{\cdot}575 \log_{10} 50{\cdot}106$

$= 184{\cdot}655$ E.U.

As before the temperature at the end of expansion is found by dropping a vertical from 3′ to cut the constant volume curve through 1. This curve lies to the right of the curve 2–3′, the horizontal intercepts being equal between the curves. This intercept is

$$m_1 \frac{R}{J} \log_e 5 = 2{\cdot}881 \times 4{\cdot}575 \log_{10} 5 = 9{\cdot}213.$$

If this amount is added to the table of entropies on p. 59, the following values are obtained for temperatures from 2000° F. abs. to 4190° F. abs. at which temperature level the vertical from 3′ meets the curve.

T	S
2000	166·698
2500	171·851
3000	176·228
3500	180·026
4000	183·383
4190	184·566.

The following table gives the details of the calculation with $T = 4190°$ F. abs.

$$P_{4'} = \frac{4190}{600} = 6{\cdot}9835 \text{ atmos.}$$

Gas	m	S_T	mS_T
CO_2	1	76·178	76·178
N_2	1·881	61·562	115·798
	$\Sigma m = 2{\cdot}881$		$\Sigma(mS_T) = 191{\cdot}976$

$$\Sigma\left(4{\cdot}575m \log_{10} \frac{\Sigma m}{m}\right) = 3{\cdot}695 \text{ as before.}$$

Hence,

S at 4190° F. abs.

$= 191{\cdot}976 + 3{\cdot}695 - 2{\cdot}881 \times 4{\cdot}575 \log_{10} 6{\cdot}9835$

$= 191{\cdot}976 + 3{\cdot}695 - 11{\cdot}125$

$= 184{\cdot}546$ (as against 184·655).

Ideal Thermal Efficiency

(*a*) *Cycle with Dissociation*

The heat supplied is the area under the curve 2–3, i.e. H_v at 1012° F. abs. or 120990 B.Th.U. The heat rejected is the area under the curve 4–1, i.e. 84268 B.Th.U.

Hence the efficiency is

$$\eta = \frac{\text{Heat supplied} - \text{Heat rejected}}{\text{Heat supplied}}$$
$$= \frac{120990 - 84268}{120990}$$
$$= 0{\cdot}3035 \text{ or } 30{\cdot}35\%.$$

(*b*) *Cycle without Dissociation*

In this case the efficiency is given by

$$\eta = \frac{(E_3 - E_2) - (E_4 - E_1)}{(E_3 - E_2)}$$

but $E_3 - E_2 = H_{v_2} = 120990$ and $E_4 - E_1$ is the difference in internal energy of the products between the temperatures 4190° F. abs. and 600° F. abs., i.e.

$$E_4 - E_1 = \Sigma m E_{4190} - \Sigma m E_{600}$$
$$= (43784 + 46461) - (3434 + 5603)$$
$$= 81208.$$

Hence the value of the efficiency is given by

$$\eta = \frac{120990 - 81208}{120990}$$
$$= 0{\cdot}3288 \text{ or } 32{\cdot}88\%.$$

The error in neglecting dissociation is thus about 8·3 per cent.

EXAMPLE 9. *Ideal attainable Efficiency of the Constant Volume Cycle using the Products from the Combustion of Benzene as the Working Substance*

Only the main results need be indicated here as the method of solution is similar to that of example 8. It is assumed that the working substance throughout the cycle consists of the products formed by the combustion of one mol of benzene with the theoretically correct air. The temperature and pressure at the beginning of compression are taken as 600° F. abs. and 1 atmosphere. The ideal cycle consists of (fig. 19):

(*a*) Isentropic compression with a compression ratio of 5;

(*b*) Heat reception at constant volume;

(*c*) Isentropic expansion;

(*d*) Heat rejection at constant volume.

The reaction equation is expressed as

$$C_6H_6+7{\cdot}5\,O_2+28{\cdot}214\,N_2 \rightarrow 6\,CO_2+3\,H_2O+28{\cdot}214\,N_2.$$

(*a*) *Compression*

The absolute entropy at the beginning of compression is found tabularly as follows :

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10}\frac{\Sigma m}{m}$	$4{\cdot}575m\log_{10}\frac{\Sigma m}{m}$
CO_2	6·000	52·104	312·624	6·2023	0·79255	21·755
H_2O	3·000	46·034	138·102	12·405	1·09360	15·010
N_2	28·214	46·574	1314·039	1·3190	0·12022	15·518

$\Sigma m=\underline{37{\cdot}214}$; $\Sigma(mS_T)=\underline{1764{\cdot}765}$; $\Sigma\left(4{\cdot}575m\log_{10}\frac{\Sigma m}{m}\right)=\underline{52{\cdot}283}$

$$S_{600}=\Sigma(mS_T)+\Sigma\left(4{\cdot}575m\log_{10}\frac{\Sigma m}{m}\right)$$
$$=1817{\cdot}048\text{ E.U.}$$

The pressure P_2 at the end of compression is found from the relationship

$$P_2V_2/T_2=P_1V_1/T_1$$

giving

$$P_2=1\times5\times T_2/600$$
$$=T_2/120.$$

By trial and error it is found that $T_2=1057°$ F. abs. satisfies the condition of equal absolute entropies at the points 1 and 2. Thus, tabulating, we have

Gas	m	S_T	mS_T
CO_2	6·000	57·893	347·358
H_2O	3·000	50·727	152·181
N_2	28·214	50·548	1426·161
		$\Sigma(mS_T)=$	1925·700

$$P_2=1057/120$$
$$=8{\cdot}8083\text{ atm.}$$

and

$$\Sigma m\,4{\cdot}575\log_{10}P_2/P_1$$
$$=37{\cdot}214\times4{\cdot}575\times0{\cdot}94489$$
$$160{\cdot}871\text{ E.U.}$$

Hence

$$S_{1057}=1925{\cdot}700+52{\cdot}283-160{\cdot}871$$
$$=1817{\cdot}112\text{ E.U.}$$

as against 1817·048 E.U. at the beginning of compression.

(*b*) *Heating at constant volume*

The énergy equation is given by

$$H_{r_2}=[6E_{CO_2}+3E_{H_2O}+28{\cdot}214E_{N_2}]_{T_2}^{T_3}+[xH_{rCO}+yH_{rH_2}+uH_{rOH}+zH_{rNO}]_{T_3},$$

where H_{r_2} is the heat of reaction of benzene at T_2, i.e. 1362140 B.Th.U./lb. mol and since the internal energies of 6 mols of CO_2,

of 3 mols of H_2O and 28·214 mols of N_2 are respectively 43464, 19548 and 149365 at $T_2=1057°$ F. abs., the energy equation becomes

$$1362140=[6E_{CO_2}+3E_{H_2O}+28{\cdot}214E_{N_2}]_{T_3}-43464-19548-149365$$
$$+[xH_{rCO}+yH_{rH_2}+uH_{rOH}+zH_{rNO}]_T$$

or

$$[xH_{rCO}+yH_{rH_2}+uH_{rOH}+zH_{rNO}]_{T_3}$$
$$=1574517-[6E_{CO_2}+3E_{H_2O}+28{\cdot}214E_{N_2}]_{T_3},$$

The equilibrium equations are

$$K_{pCO_2}=\frac{6-x}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}}\left(\frac{m_2T_2}{P_2T_3}\right)^{\frac{1}{2}},$$

$$K_{p\text{w.g.}}=\frac{(3-u-y)x}{(6-x)(y+0{\cdot}5u)},$$

$$K_{pOH}=\frac{3-u-y}{u(y+0{\cdot}5u)^{\frac{1}{2}}}\left(\frac{m_2T_2}{P_2T_3}\right)^{\frac{1}{2}},$$

$$K_{pNO}=\frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}},$$

and with $T_2=1057°$ F. abs., $P_2=8{\cdot}8083$ atmospheres and $m_2=37{\cdot}214$ mols, these equations become

$$K_{pCO_2}=\frac{66{\cdot}827(6-x)}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}}\cdot\frac{1}{T_3^{\frac{1}{2}}}\quad\ldots\ldots\text{I}$$

$$K_{p\text{w.g.}}=\frac{(3-u-y)x}{(6-x)(y+0.5u)}\quad\ldots\ldots\text{II}$$

$$K_{pOH}=\frac{66{\cdot}827(3-u-y)}{u(y+0{\cdot}5u)^{\frac{1}{2}}}\cdot\frac{1}{T_3^{\frac{1}{2}}}\quad\ldots\ldots\text{III}$$

$$K_{pNO}=\frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}}\quad\ldots\ldots\text{IV}$$

By trial and error it is found that the above equations are all satisfied at $T_3=5215°$ F. abs. Thus at this temperature the values of $6E_{CO_2}$, $3E_{H_2O}$ and $28{\cdot}214E_{N_2}$ are 341946, 138231 and 893340, so that the right-hand side of the energy equation given on p. 62 is equal to

$$1574517-(341946+138231+893340)$$
$$=201000\text{ B.Th.U.}$$

The corresponding values of H_{rCO}, H_{rH_2}, H_{rOH} and H_{rNO} are 112065, 103386, 119673 and 38647. The energy equation thus becomes

$$112065x+103386y+119673u+38647z=201000,$$

so that

$$z=5{\cdot}200915-2{\cdot}899704x-2{\cdot}675133y-3{\cdot}096563u.$$

The equilibrium constants at $T_3=5215°$ F. abs. are

$$K_{p_{CO_2}}=4{\cdot}2806\,;\quad K_{p_{w.g.}}=7{\cdot}4166\,;\quad K_{p_{OH}}=31{\cdot}146\,;\quad K_{p_{NO}}=0{\cdot}10818,$$

so that

$$4{\cdot}2806=\frac{66{\cdot}827\,(6-x)}{x\,(0{\cdot}5x+0{\cdot}5y-2{\cdot}600457+1{\cdot}449852x+1{\cdot}337567y+1{\cdot}548282u)^{\frac{1}{2}}\times 72{\cdot}215}$$

giving

$$4{\cdot}6257=\frac{(6-x)}{x\,(1{\cdot}949852x+1{\cdot}837567y+1{\cdot}548282u-2{\cdot}600457)^{\frac{1}{2}}}\;\ldots\ldots\mathrm{I}\;(a)$$

$$7{\cdot}4166=\frac{(3-u-y)\,x}{(6-x)\,((y+0{\cdot}5u)}\;\ldots\ldots\mathrm{II}\;(a)$$

$$31{\cdot}146=\frac{66{\cdot}827\,(3-u-y)}{u\,(y+0{\cdot}5u)^{\frac{1}{2}}\,72{\cdot}215}$$

giving

$$33{\cdot}657=\frac{3-u-y}{u\,(y+0{\cdot}5u)^{\frac{1}{2}}},\;\ldots\ldots\mathrm{III}\;(a)$$

$$0{\cdot}10818=\frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}\,(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}}\;\ldots\ldots\mathrm{IV}\;(a)$$

With a finally assumed value of $u=0{\cdot}2437$ equation III (a) gives $y=-0{\cdot}00823$,

so that

$$7{\cdot}4166=\frac{2{\cdot}76453x}{(6-x)\,0{\cdot}11362}$$

from which $x=1{\cdot}40165$.

The right-hand side of equation I (a) then equals 4·6641 as against 4·6257 on the left-hand side. Accepting these values therefore for x, y and u and inserting them in the energy equation gives

$$z=5{\cdot}20092-4{\cdot}06437+0{\cdot}02202-0{\cdot}75463$$
$$=0{\cdot}40394.$$

The right-hand side of equation IV (a) then becomes

$$\frac{0{\cdot}40394}{5{\cdot}2926\times 0{\cdot}70339}=0{\cdot}10851$$

as against 0·10818 on the left-hand side so that the assumed values may be accepted.

The table below, which is drawn up for the purpose of calculating the entropy of the products at the end of the constant volume burning period, i.e. at the point 3, also shows the composition of the dissociated products at that point.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10}\frac{\Sigma m}{m}$	$4{\cdot}575m\log_{10}\frac{\Sigma m}{m}$
CO_2	4·59835	79·425	365·224	8·2709	0·91756	19·303
CO	1·40165	65·170	91·345	27·134	1·43350	9·192
H_2O	2·76453	68·061	188·157	13·757	1·13852	14·400
H_2	0·11362	48·166	5·473	334·73	2·52470	1·312
OH	0·24370	61·091	14·888	156·06	2·19329	2·445
O_2	0·49475	67·661	33·475	76·872	1·88577	4·268
NO	0·40394	68·563	27·695	94·154	1·97384	3·648
N_2	28·01203	63·483	1778·288	1·3577	0·13276	17·014

$\Sigma m = 38{\cdot}03257$; $\Sigma(mS_T) = 2504{\cdot}545$; $\Sigma\left(4{\cdot}575m\log_{10}\frac{\Sigma m}{m}\right) = 71{\cdot}582$

$$P_3 = \frac{8{\cdot}8083 \times 38{\cdot}03257 \times 5215}{37{\cdot}214 \times 1057}$$

$$= 44{\cdot}414 \text{ atmospheres.}$$

$$S_{5215} = 2504{\cdot}545 + 71{\cdot}582 - 38{\cdot}03257 \times 4{\cdot}575 \log_{10} 44{\cdot}414$$

$$= 2289{\cdot}460 \text{ E.U.}$$

The state point at the end of constant volume burning can thus be located on the TS field but, in order to represent the constant volume combustion curve, it is necessary to determine the entropies of the equilibrium mixtures at various temperature levels. At any temperature T the equilibrium constants are expressed by the relationships:

$$K_{pCO_2} = \frac{66{\cdot}827(6-x)}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \cdot \frac{1}{T^{\frac{1}{2}}} \quad \ldots\ldots \text{I}$$

$$K_{p\text{w.g.}} = \frac{(3-u-y)x}{(6-x)(y+0{\cdot}5u)} \quad \ldots\ldots \text{II}$$

$$K_{pOH} = \frac{66{\cdot}827(3-u-y)}{u(y+0{\cdot}5u)^{\frac{1}{2}}} \cdot \frac{1}{T^{\frac{1}{2}}} \quad \ldots\ldots \text{III}$$

$$K_{pNO} = \frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \ldots\ldots \text{IV}$$

At 4500° F. abs. these become

$$26{\cdot}303 = \frac{66{\cdot}827(6-x)}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}} \times 67{\cdot}082},$$

so that

$$26{\cdot}403 = \frac{6-x}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)} \quad \ldots\ldots \text{I}\,(a)$$

$$6{\cdot}422 = \frac{(3-u-y)x}{(6-x)(y+0{\cdot}5u)} \quad \ldots\ldots \text{II}\,(a)$$

$$211{\cdot}4 = \frac{66{\cdot}827(3-u-y)}{u(y+0{\cdot}5u)^{\frac{1}{2}} \times 67{\cdot}082},$$

so that

$$212{\cdot}21 = \frac{3-u-y}{u(y+0{\cdot}5u)^{\frac{1}{2}}} \quad \ldots\ldots \text{III}\,(a)$$

$$0{\cdot}059759 = \frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \ldots\ldots \text{IV}\,(a)$$

By trial and error it is found that $u=0\cdot0685$ and equation III (*a*) then gives $y=0\cdot00625$. Equation II (*a*) then gives $x=0\cdot48992$ and equation I (*a*) gives $z=0\cdot13327$. Inserting these values in the right-hand side of equation IV (*a*) gives 0·05897 as against 0·05976 on the left-hand side. The composition of the products of combustion at 4500° F. abs. is as shown in the following table which has been drawn up for the purpose of calculating the entropy of the mixture at this condition.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10}\frac{\Sigma m}{m}$	$4\cdot575m\log_{10}\frac{\Sigma m}{m}$
CO_2	5·51008	77·230	425·543	6·8050	0·83283	20·994
CO	0·48992	63·866	31·289	76·536	1·88386	4·222
H_2O	2·92525	66·127	193·438	12·818	1·10782	14·826
H_2	0·04050	46·891	1·899	925·84	2·96654	0·550
OH	0·06850	59·803	4·097	547·39	2·73830	0·858
O_2	0·18146	66·278	12·027	206·64	2·31522	1·922
NO	0·13327	67·248	8·962	281·36	2·44926	1·493
N_2	28·14737	62·186	1750·372	1·3321	0·12454	16·038

$\Sigma m=37\cdot49635$; $\Sigma(mS_T)=2427\cdot627$; $\Sigma\left(4\cdot575m\log_{10}\frac{\Sigma m}{m}\right)=60\cdot903$

The pressure at this state point is given by the expression

$$P_{4500}=\frac{4500\times37\cdot49635\,P_2}{m_2T_2}$$
$$=\frac{4500\times37\cdot49635\times8\cdot8083}{37\cdot214\times1057}$$
$$=37\cdot784 \text{ atmospheres.}$$

The entropy at this point is therefore

$$S_{4500}=2427\cdot627+60\cdot903-37\cdot49635\times4\cdot575\times1\cdot57732$$
$$=2217\cdot947 \text{ E.U.}$$

Repeating the calculation in the same way with $T=4000°$ F. abs. gives $P=33\cdot422$ atmospheres and $S=2171\cdot604$ E.U.

In order that the constant volume curve may be drawn on the TS field it is necessary to calculate the entropies for a series of temperatures ranging from 1057° F. abs. (the temperature at the end of compression) to 3500° F. abs. Up to this temperature it may be assumed that the degree of dissociation is negligible. At 1500° F. abs. the entropy is found tabularly as follows:

Gas	m	S_T	mS_T
CO_2	6·000	62·048	372·288
H_2O	3·000	53·881	161·643
N_2	28·214	53·130	1499·010

$\Sigma m=37\cdot214$; $\Sigma(mS_T)=2032\cdot941$

$$P_{1500}=\frac{8\cdot8083\times1500}{1057}$$
$$=12\cdot5 \text{ atmospheres.}$$
$$S_{1500}=2032\cdot941+52\cdot283-186\cdot753$$
$$=1898\cdot471 \text{ E.U.}$$

The entropies at a series of progressively increasing temperatures are calculated in the same way and tabulated below.

$T=$ 1500	2000	2500	3000	3500
$S=$1898·47	1970·86	2030·68	2081·68	2126·11

Dealing now with the constant cooling curve 4 – 1, the entropy at the temperature level T is given by the expression

$$\Sigma m S_T - \Sigma m\ 4{\cdot}575 \log_{10} \frac{P_{1000}}{P_{600}} + \Sigma m\ 4{\cdot}575 \log_{10} \frac{\Sigma m}{m},$$

and with $T=1000°$ F. abs.

$$\Sigma m S_T = 6{\cdot}000 \times 57{\cdot}284 + 3{\cdot}000 \times 50{\cdot}257 + 28{\cdot}214 \times 50{\cdot}158$$
$$= 1909{\cdot}633 \text{ E.U.}$$

also, from S_{600} as given on p. 62

$$\Sigma m\ 4{\cdot}575 \log_{10} \frac{\Sigma m}{m} = 52{\cdot}283 \text{ E.U.}$$

The value of P_{1000} is $1000/600 = 1{\cdot}6667$ atmospheres, so that

$$\Sigma m\ 4{\cdot}575 \log_{10} 1{\cdot}6667/1$$
$$= 37{\cdot}214 \times 4{\cdot}575 \times 0{\cdot}22186$$
$$= 37{\cdot}771 \text{ E.U.}$$

We therefore have

$$S_{1000} = 1909{\cdot}633 + 52{\cdot}283 - 37{\cdot}771$$
$$= 1924{\cdot}145 \text{ E.U.}$$

The table below gives the values of the entropies at various temperature levels up to 3000° F. abs., obtained by adding

$$\Sigma m \frac{R}{J} \log_e 5 = 37{\cdot}214 \times 4{\cdot}575 \times 0{\cdot}69897 = 119{\cdot}002 \text{ E.U.}$$

to the corresponding entropy values in the table above for the curve 2 – 3.

$T°$ F. abs.	S
600	1817·048
1000	1924·145
1500	2017·473
2000	2089·864
2500	2149·683
3000	2200·683

At temperatures above 3000° F. abs. the dissociation effects may no longer be neglected so that the method already explained for determining the true composition of the dissociated products has again to be adopted. The equilibrium constants are as follows:

$$K_{pCO_2} = \frac{6-x}{x(0{\cdot}5x + 0{\cdot}5y - 0{\cdot}5z)^{\frac{1}{2}}} \left(\frac{m_1 T_1}{P_1 T_4}\right)^{\frac{1}{2}} \ldots\ldots\ldots\ldots \text{I}\,(b)$$

$$K_{p_{\mathrm{w.g.}}}=\frac{(3-u-y)x}{(6-x)(y+0{\cdot}5u)} \quad \ldots\ldots \text{II}\,(b)$$

$$K_{p_{\mathrm{OH}}}=\frac{3-u-y}{u(y+0{\cdot}5u)^{\frac{1}{2}}}\left(\frac{m_1T_1}{P_1T_4}\right)^{\frac{1}{2}} \quad \ldots\ldots \text{III}\,(b)$$

$$K_{p_{\mathrm{NO}}}=\frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}\,(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \ldots\ldots \text{IV}\,(b)$$

Substituting for m_1, T_1 and P_1 gives

$$K_{p_{\mathrm{CO_2}}}=\frac{149{\cdot}43(6-x)}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}}\cdot\frac{1}{T_4^{\frac{1}{2}}} \quad \ldots\ldots \text{I}\,(c)$$

$$K_{p_{\mathrm{w.g.}}}=\frac{(3-u-y)x}{(6-x)(y+0{\cdot}5u)} \quad \ldots\ldots \text{II}\,(c)$$

$$K_{p_{\mathrm{OH}}}=\frac{149{\cdot}43(3-u-y)}{u(y+0{\cdot}5u)^{\frac{1}{2}}\times T_4^{\frac{1}{2}}} \quad \ldots\ldots \text{III}\,(c)$$

$$K_{p_{\mathrm{NO}}}=\frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}\,(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \ldots\ldots \text{IV}\,(c)$$

At $T_4=3500°$ F. abs. the above equations become

$$1180{\cdot}3=\frac{149{\cdot}43(6-x)}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}\times 59{\cdot}161}$$

which gives

$$467{\cdot}29=\frac{6-x}{x(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \ldots\ldots \text{I}\,(d)$$

$$4{\cdot}549=\frac{(3-u-y)x}{(6-x)(y+0{\cdot}5u)} \quad \ldots\ldots \text{II}\,(d)$$

$$11390=\frac{149{\cdot}43(3-u-y)}{u(y+0{\cdot}5u)^{\frac{1}{2}}\times 59{\cdot}161},$$

which gives

$$4509=\frac{3-u-y}{u(y+0{\cdot}5u)^{\frac{1}{2}}} \quad \ldots\ldots \text{III}\,(d)$$

$$0{\cdot}017282=\frac{z}{(28{\cdot}214-0{\cdot}5z)^{\frac{1}{2}}\,(0{\cdot}5x+0{\cdot}5y-0{\cdot}5z)^{\frac{1}{2}}} \quad \ldots\ldots \text{IV}\,(d)$$

Solving these four equations in the way already explained gives the following values :

$$x=0{\cdot}072560$$
$$y=0{\cdot}004350$$
$$z=0{\cdot}015789$$
$$u=0{\cdot}007390$$

from which $P_{3500}=5{\cdot}8400$ atmospheres.

$S_{3500}=2248{\cdot}355$ E.U.

It will be found that at $T_4=3930°$ F abs. the entropy of the products

is the same as that at the beginning of expansion and at this temperature the following values are obtained :

$$x = 0{\cdot}241830$$
$$y = 0{\cdot}008400$$
$$z = 0{\cdot}052969$$
$$u = 0{\cdot}029100$$

from which $P_{3930} = 6{\cdot}5746$ atmospheres,
$S_{3930} = 2288{\cdot}765$ E.U.

Thermal Efficiency

The heat supplied under the conditions stated above, i.e. when dissociation is taken into account, is given by the area under the curve 2 – 3, while the heat rejected is given by the area under the curve 4 – 1.

Area under curve 2 – 3 is H_{r_2}

$$= 1362140 \text{ B.Th.U.}$$

Area under curve 4 – 1

$$= 907918 \text{ B.Th.U.}$$

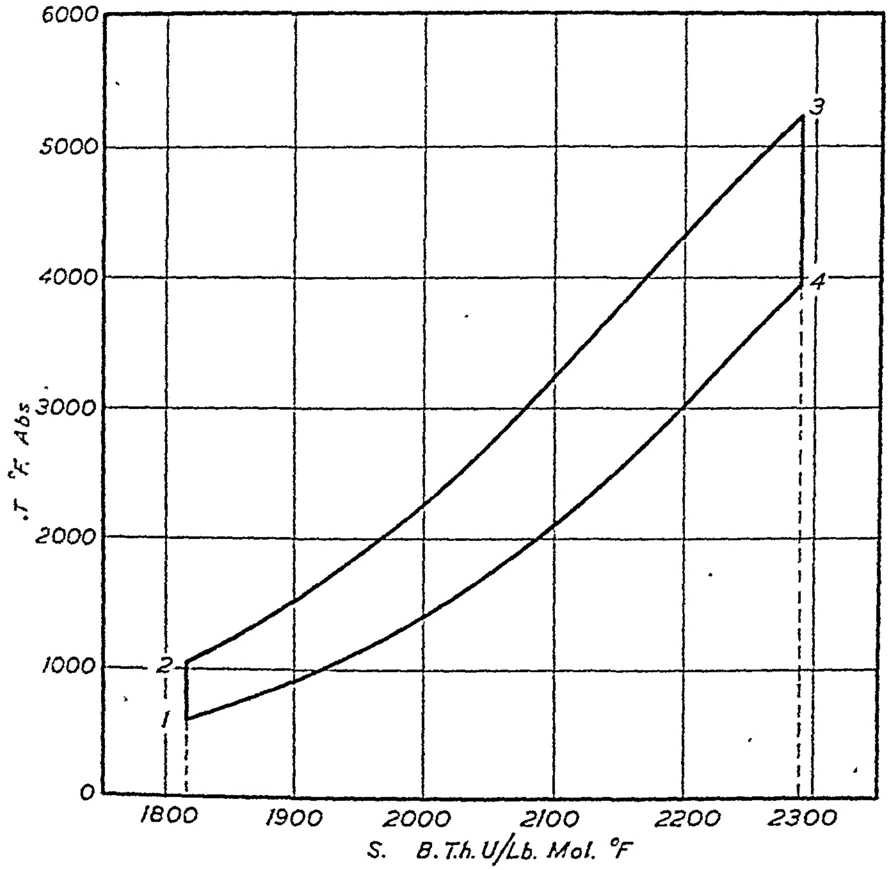

FIG. 19.

Hence the ideal efficiency is

$$=\frac{1362140-907918}{1362140}$$
$$=0{\cdot}3335 \text{ or } 33{\cdot}35\%.$$

It is not possible in this case to determine accurately the ideal efficiency of this cycle when no dissociation occurs as the maximum temperature is then above 5400° F. abs., which is the upper limit of temperature for which properties of H_2O are available.

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TABLES

SYMBOLS USED IN TABLES

E Internal Energy, B.Th.U./lb. mol.

$-\frac{F}{T}$ Function of Free Energy, B.Th.U./lb. mol ° F.

H Total Heat, B.Th.U./lb. mol.

H_v Lower Heat of Reaction at Constant Volume, B.Th.U./lb. mol.

H_p Lower Heat of Reaction at Constant Pressure, B.Th.U./lb. mol.

K_p Equilibrium Constant.

S Entropy, B.Th.U./lb. mol ° F.

ΔE_0 Heat of Reaction at Absolute Zero Temperature.

$\frac{R}{J} = 1{\cdot}9869$ B.Th.U./lb. mol ° F.

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OXYGEN

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
100									100
200									200
300									300
400	46·996	1·527	1985	489	2780	687	40·045	1·545	400
500	48·523	1·293	2474	502	3467	711	41·590	1·281	500
600	49·816	1·097	2976	515	4168	713	42·871	1·070	600
700	50·913	0·965	3491	525	4881	724	43·941	0·930	700
800	51·878	0·866	4016	537	5605	736	44·871	0·827	800
900	52·744	0·789	4553	551	6341	750	45·698	0·744	900
1000	53·533	0·727	5104	565	7091	764	46·442	0·677	1000
1100	54·260	0·675	5669	578	7855	776	47·119	0·623	1100
1200	54·935	0·630	6247	589	8631	788	47·742	0·578	1200
1300	55·565	0·592	6836	600	9419	799	48·320	0·539	1300
1400	56·157	0·557	7436	609	10218	807	48·859	0·505	1400
1500	56·714	0·526	8045	618	11025	817	49·364	0·475	1500
1600	57·240	0·499	8663	625	11842	824	49·839	0·450	1600
1700	57·739	0·475	9288	632	12666	830	50·289	0·427	1700
1800	58·214	0·453	9920	639	13496	838	50·716	0·407	1800
1900	58·667	0·433	10559	645	14334	344	51·123	0·388	1900
2000	59·100	0·413	11204	650	15178	848	51·511	0·370	2000
2100	59·513	0·397	11854	653	16026	852	51·881	0·358	2100
2200	59·910	0·380	12507	657	16878	856	52·239	0·340	2200
2300	60·290	0·367	13164	662	17734	860	52·579	0·331	2300
2400	60·657	0·352	13826	665	18594	864	52·910	0·316	2400
2500	61·009	0·341	14491	669	19458	868	53·226	0·307	2500
2600	61·350	0·329	15160	673	20326	872	53·533	0·295	2600
2700	61·679	0·319	15833	678	21198	876	53·828	0·286	2700
2800	61·998	0·308	16511	680	22074	879	54·114	0·277	2800
2900	62·306	0·299	17191	684	22953	883	54·391	0·268	2900
3000	62·605	0·291	17875	687	23836	885	54·659	0·262	3000
3100	62·896	0·282	18562	690	24721	889	54·921	0·254	3100
3200	63·178	0·275	19252	693	25610	892	55·175	0·247	3200
3300	63·453	0·267	19945	697	26502	895	55·422	0·240	3300
3400	63·720	0·260	20642	700	27397	899	55·662	0·233	3400
3500	63·980	0·254	21342	703	28296	902	55·895	0·228	3500
3600	64·234	0·249	22045	707	29198	905	56·123	0·224	3600
3700	64·483	0·242	22752	710	30103	909	56·347	0·217	3700
3800	64·725	0·236	23462	711	31012	910	56·564	0·212	3800
3900	64·961	0·231	24173	714	31922	913	56·776	0·207	3900
4000	65·192	0·227	24887	718	32835	916	56·983	0·203	4000
4100	65·419	0·221	25605	720	33751	919	57·186	0·200	4100
4200	65·640	0·217	26325	723	34670	922	57·386	0·194	4200
4300	65·857	0·213	27048	726	35592	924	57·580	0·190	4300
4400	66·070	0·208	27774	727	36516	926	57·770	0·187	4400
4500	66·278	0·204	28501	731	37442	930	57·957	0·183	4500

OXYGEN (*continued*)

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
4600	66·482	0·201	29232	735	38372	933	58·140	0·181	4600
4700	66·683	0·197	29967	738	39305	937	58·321	0·174	4700
4800	66·880	0·194	30705	740	40242	939	58·495	0·174	4800
4900	67·074	0·190	31445	743	41181	942	58·669	0·170	4900
5000	67·264	0·187	32188	745	42123	943	58·839	0·168	5000
5100	67·451	0·183	32933	747	43066	946	59·007	0·164	5100
5200	67·634	0·181	33680	749	44012	948	59·171	0·161	5200
5300	67·815	0·178	34429	750	44960	948	59·332	0·161	5300
5400	67·993	0·175	35179	753	45908	952	59·493	0·156	5400
5500	68·168	0·172	35932	756	46860	955	59·649	0·152	5500
5600	68·340	0·170	36688	760	47815	958	59·801	0·151	5600
5700	68·510	0·167	37488	762	48773	961	59·952	0·149	5700
5800	68·677	0·165	38210	765	49734	964	60·101	0·147	5800
5900	68·842	0·162	38975	769	50698	967	60·248	0·145	5900
6000	69·004	0·160	39744	771	51665	970	60·393	0·142	6000
6100	69·164	0·158	40515	773	52635	972	60·535	0·141	6100
6200	69·322	0·156	41288	777	53607	975	60·676	0·138	6200
6300	69·478	0·154	42065	777	54582	976	60·814	0·137	6300
6400	69·632	0·151	42848	778	55558	977	60·951	0·136	6400
6500	69·783	0·149	43620	779	56535	978	61·087	0·133	6500
6600	69·932	0·147	44399	782	57513	980	61·220	0·130	6600
6700	70·079	0·145	45181	782	58493	981	61·350	0·129	6700
6800	70·224	0·144	45963	784	59474	983	61·479	0·128	6800
6900	70·368	0·141	46747	786	60457	984	61·607	0·126	6900
7000	70·509	0·140	47533	786	61441	985	61·733	0·125	7000
7100	70·649	0·138	48319	788	62426	987	61·858	0·122	7100
7200	70·787	0·137	49107	791	63413	989	61·980	0·122	7200
7300	70·924	0·135	49898	791	64402	990	62·102	0·121	7300
7400	71·059	0·133	50689	793	65392	992	62·223	0·118	7400
7500	71·192	0·132	51482	796	66384	994	62·341	0·117	7500
7600	71·324	0·130	52278	797	67378	996	62·458	0·116	7600
7700	71·454	0·128	53075	799	68374	998	62·574	0·115	7700
7800	71·582	0·127	53874	800	69372	999	62·689	0·114	7800
7900	71·709	0·126	54674	802	70371	1000	62·803	0·112	7900
8000	71·835	0·124	55476	802	71371	1001	62·915	0·111	8000
8100	71·959	0·123	56278	804	72372	1003	63·026	0·109	8100
8200	72·082	0·121	57082	805	73375	1003	63·135	0·108	8200
8300	72·203	0·120	57887	806	74378	1005	63·243	0·107	8300
8400	72·323	0·119	58693	806	75383	1005	63·350	0·106	8400
8500	72·442	0·118	59499	808	76388	1006	63·456	0·105	8500
8600	72·560	0·116	60307	809	77394	1008	63·561	0·104	8600
8700	72·676	0·115	61116	810	78402	1008	63·665	0·103	8700
8800	72·791	0·114	61926	810	79411	1009	63·768	0·101	8800
8900	72·905	0·113	62736	811	80420	1009	63·869	0·101	8900
9000	73·018		63547		81429		63·970		9000

NITROGEN (*continued*)

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
4600	62·378	0·189	27471	679	36611	877	54·419	0·173	4600
4700	62·567	0·185	28150	680	37488	879	54·592	0·166	4700
4800	62·752	0·182	28830	681	38367	880	54·758	0·166	4800
4900	62·934	0·178	29511	682	39247	881	54·924	0·162	4900
5000	63·112	0·175	30193	683	40128	881	55·086	0·160	5000
5100	63·287	0·171	30876	684	41009	883	55·246	0·157	5100
5200	63·458	0·169	31560	685	41892	884	55·403	0·153	5200
5300	63·627	0·165	32245	686	42776	885	55·556	0·152	5300
5400	63·792	0·163	32931	687	43661	885	55·708	0·148	5400
5500	63·955	0·160	33618	688	44546	887	55·856	0·146	5500
5600	64·115	0·157	34306	689	45433	888	56·002	0·144	5600
5700	64·272	0·154	34995	690	46321	888	56·146	0·140	5700
5800	64·426	0·152	35685	690	47209	889	56·286	0·139	5800
5900	64·578	0·150	36375	692	48098	890	56·425	0·138	5900
6000	64·728	0·147	37067	692	48988	891	56·563	0·135	6000
6100	64·875	0·145	37759	693	49879	892	56·698	0·133	6100
6200	65·020	0·143	38452	695	50771	893	56·831	0·131	6200
6300	65·163	0·141	39147	695	51664	894	56·962	0·130	6300
6400	65·304	0·139	39842	696	52558	895	57·092	0·129	6400
6500	65·443	0·137	40538	697	53453	896	57·221	0·126	6500
6600	65·580	0·135	41235	697	54349	896	57·347	0·124	6600
6700	65·715	0·133	41932	698	55245	896	57·471	0·121	6700
6800	65·848	0·130	42630	698	56141	897	57·592	0·121	6800
6900	65·978	0·129	43328	700	57038	898	57·713	0·119	6900
7000	66·107	0·127	44028	700	57936	899	57·832	0·117	7000
7100	66·234	0·126	44728	700	58835	899	57·949	0·116	7100
7200	66·360	0·124	45428	702	59734	900	58·065	0·115	7200
7300	66·484	0·123	46130	702	60634	901	58·180	0·114	7300
7400	66·607	0·122	46832	703	61535	902	58·294	0·111	7400
7500	66·729	0·120	47535	704	62437	902	58·405	0·110	7500
7600	66·849	0·118	48239	704	63339	903	58·515	0·110	7600
7700	66·967	0·117	48943	704	64242	903	58·625	0·109	7700
7800	67·084	0·115	49647	704	65145	903	58·734	0·107	7800
7900	67·199	0·114	50351	704	66048	903	58·841	0·106	7900
8000	67·313	0·112	51055	704	66951	903	58·947	0·103	8000
8100	67·425	0·110	51759	705	67854	903	59·050	0·102	8100
8200	67·535	0·108	52464	705	68757	903	59·152	0·100	8200
8300	67·643	0·107	53169	705	69660	904	59·252	0·100	8300
8400	67·750	0·106	53874	705	70564	904	59·352	0·099	8400
8500	67·856	0·105	54579	706	71468	904	59·451	0·098	8500
8600	67·961	0·105	55285	706	72372	905	59·549	0·097	8600
8700	68·066	0·104	55991	707	73277	906	59·646	0·096	8700
8800	68·170	0·102	56698	708	74183	906	59·742	0·093	8800
8900	68·272	0·101	57406	708	75089	907	59·835	0·093	8900
9000	68·373		58114		75996		59·928		9000

CARBON DIOXIDE

T° F. Abs.	S		E		H		$-\frac{\Gamma}{T}$		T° F. Abs.
100									100
200									200
300									300
400	48·620	1·853	2100	636	2895	834	41·383	1·633	400
500	50·473	1·631	2736	698	3729	897	43·016	1·378	500
600	52·104	1·465	3434	751	4626	949	44·394	1·211	600
700	53·569	1·337	4185	803	5575	1002	45·605	1·080	700
800	54·906	1·233	4988	847	6577	1046	46·685	0·983	800
900	56·139	1·145	5835	887	7623	1086	47·668	0·907	900
1000	57·284	1·068	6722	916	8709	1115	48·575	0·846	1000
1100	58·352	1·004	7638	959	9824	1157	49·421	0·784	1100
1200	59·356	0·946	8597	982	10981	1181	50·205	0·742	1200
1300	60·302	0·896	9579	1009	12162	1208	50·947	0·701	1300
1400	61·198	0·850	10588	1033	13370	1231	51·648	0·666	1400
1500	62·048	0·810	11621	1055	14601	1254	52·314	0·635	1500
1600	62·858	0·773	12676	1074	15855	1273	62·949	0·607	1600
1700	63·631	0·739	13750	1093	17128	1291	53·556	0·582	1700
1800	64·370	0·708	14843	1110	18419	1309	54·138	0·557	1800
1900	65·078	0·678	15953	1125	19728	1324	54·695	0·535	1900
2000	65·756	0·652	17078	1138	21052	1336	55·230	0·517	2000
2100	66·408	0·627	18216	1149	22388	1348	55·747	0·499	2100
2200	67·035	0·604	19365	1160	23736	1359	56·246	0·482	2200
2300	67·639	0·582	20525	1170	25095	1368	56·728	0·467	2300
2400	68·221	0·563	21695	1181	26463	1380	57·195	0·452	2400
2500	68·784	0·545	22876	1189	27843	1388	57·647	0·440	2500
2600	69·329	0·527	24065	1197	29231	1396	58·087	0·425	2600
2700	69·856	0·510	25262	1205	30627	1403	58·512	0·414	2700
2800	70·366	0·495	26467	1213	32030	1412	58·926	0·404	2800
2900	70·861	0·481	27680	1219	33442	1418	59·330	0·391	2900
3000	71·342	0·467	28899	1224	34860	1422	59·721	0·384	3000
3100	71·809	0·454	30123	1230	36282	1429	60·105	0·373	3100
3200	72·263	0·441	31353	1235	37711	1434	60·478	0·364	3200
3300	72·704	0·430	32588	1242	39145	1440	60·842	0·355	3300
3400	73·134	0·419	33830	1246	40585	1445	61·197	0·347	3400
3500	73·553	0·408	35076	1248	42030	1447	61·544	0·341	3500
3600	73·961	0·397	36324	1254	43477	1452	61·885	0·330	3600
3700	74·358	0·389	37578	1260	44929	1459	62·215	0·325	3700
3800	74·747	0·379	38838	1263	46388	1462	62·540	0·317	3800
3900	75·126	0·370	40101	1266	47850	1465	62·857	0·310	3900
4000	75·496	0·362	41367	1270	49315	1468	63·167	0·304	4000
4100	75·858	0·355	42637	1274	50783	1473	63·471	0·301	4100
4200	76·213	0·346	43911	1276	52256	1475	63·772	0·292	4200
4300	76·559	0·339	45187	1278	53731	1476	64·064	0·286	4300
4400	76·898	0·332	46465	1281	55207	1480	64·350	0·282	4400
4500	77·230	0·325	47746	1283	56687	1482	64·632	0·277	4500

CARBON DIOXIDE (*continued*)

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
4600	77·555	0·319	49029	1286	58169	1484	64·909	0·274	4600
4700	77·874	0·313	50315	1291	59653	1490	65·183	0·265	4700
4800	78·187	0·307	51606	1294	61143	1493	65·448	0·263	4800
4900	78·494	0·300	52900	1297	62636	1496	65·711	0·257	4900
5000	78·794	0·297	54197	1299	64132	1497	65·968	0·255	5000
5100	79·091	0·291	55496	1300	65629	1499	66·223	0·250	5100
5200	79·382	0·285	56796	1301	67128	1500	66·473	0·245	5200
5300	79·667	0·280	58097	1303	68628	1501	66·718	0·244	5300
5400	79·947	0·275	59400	1303	70129	1501	66·962	0·238	5400
5500	80·222	0·271	60703	1304	71630	1503	67·200	0·233	5500
5600	80·493	0·266	62007	1306	73133	1505	67·433	0·232	5600
5700	80·759	0·262	63313	1308	74638	1507	67·665	0·226	5700
5800	81·021	0·258	64621	1310	76145	1509	67·891	0·226	5800
5900	81·279	0·254	65931	1313	77654	1511	68·117	0·222	5900
6000	81·533	0·250	67244	1314	79165	1513	68·339	0·217	6000
6100	81·783	0·246	68558	1316	80678	1515	68·556	0·216	6100
6200	82·029	0·243	69874	1319	82193	1517	68·772	0·213	6200
6300	82·272		71193		83710		68·985		6300

WATER VAPOUR

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
100									100
200									200
300									300
400	42·799	1·779	2405	602	3200	798	34·800	1·778	400
500	44·578	1·456	3007	608	3998	800	36·578	1·459	500
600	46·034	1·251	3615	615	4798	813	38·037	1·233	600
700	47·285	1·097	4230	624	5611	823	39·270	1·070	700
800	48·382	0·981	5854	635	6434	834	40·340	0·947	800
900	49·363	0·894	5489	641	7268	849	41·287	0·853	900
1000	50·257	0·824	6130	677	8117	865	42·140	0·776	1000
1100	51·081	0·766	6807	682	8982	881	42·916	0·712	1100
1200	51·847	0·717	7489	697	9863	896	43·628	0·660	1200
1300	52·564	0·676	8186	715	10759	913	44·288	0·615	1300
1400	53·240	0·641	8901	731	11672	929	44·903	0·578	1400
1500	53·881	0·610	9632	747	12601	946	45·481	0·543	1500
1600	54·491	0·583	10379	764	13547	963	46·024	0·515	1600
1700	55·074	0·561	11143	782	14510	980	46·539	0·490	1700
1800	55·635	0·539	11925	799	15490	997	47·029	0·468	1800
1900	56·174	0·521	12724	816	16487	1015	47·497	0·447	1900
2000	56·695	0·503	13540	835	17502	1033	47·944	0·428	2000
2100	57·198	0·488	14375	850	18535	1050	48·372	0·412	2100
2200	57·686	0·473	15225	866	19585	1063	48·784	0·397	2200
2300	58·159	0·460	16091	880	20648	1079	49·181	0·385	2300
2400	58·619	0·446	16971	896	21727	1094	49·566	0·371	2400
2500	59·065	0·434	17867	908	22821	1107	49·937	0·360	2500
2600	59·499	0·423	18775	923	23928	1122	50·297	0·347	2600
2700	59·922	0·412	19698	934	25050	1132	50·644	0·339	2700
2800	60·334	0·403	20632	951	26182	1149	50·983	0·330	2800
2900	60·737	0·392	21583	960	27331	1159	51·313	0·319	2900
3000	61·129	0·384	22543	972	28490	1170	51·632	0·313	3000
3100	61·513	0·376	23515	984	29660	1183	51·945	0·306	3100
3200	61·889	0·368	24499	994	30843	1193	52·251	0·298	3200
3300	62·257	0·359	25493	1007	32036	1205	52·549	0·291	3300
3400	62·616	0·352	26500	1016	33241	1214	52·840	0·283	3400
3500	62·968	0·345	27516	1026	34455	1225	53·123	0·279	3500
3600	63·313	0·337	28542	1033	35680	1232	53·402	0·272	3600
3700	63·650	0·331	29575	1044	36912	1242	53·674	0·267	3700
3800	63·981	0·325	30619	1051	38154	1249	53·941	0·262	3800
3900	64·306	0·318	31670	1057	39403	1256	54·203	0·256	3900
4000	64·624	0·312	32727	1065	40659	1263	54·459	0·252	4000
4100	64·936	0·306	33792	1070	41922	1269	54·711	0·249	4100
4200	65·242	0·300	34862	1078	43191	1276	54·960	0·241	4200
4300	65·542	0·294	35940	1083	44467	1282	55·201	0·237	4300
4400	65·836	0·291	37023	1090	45749	1289	55·438	0·235	4400
4500	66·127	0·284	38113	1097	47038	1295	55·673	0·230	4500

WATER VAPOUR (*continued*)

T° F. Abs.	S		E		H		$-\frac{F}{T}$		T° F. Abs.
4600	66·411	0·280	39210	1103	48333	1302	55·903	0·228	4600
4700	66·691	0·275	40313	1110	49635	1308	56·131	0·221	4700
4800	66·966	0·271	41423	1114	50943	1313	56·352	0·220	4800
4900	67 237	0·266	42537	1119	52256	1317	56·572	0·216	4900
5000	67·503	0·262	43656	1124	53573	1322	56·788	0·214	5000
5100	67·765	0·258	44780	1127	54895	1326	57·002	0·210	5100
5200	68·023	0·253	45907	1131	56221	1330	57·212	0·206	5200
5300	68·276	0·249	47038	1136	57551	1334	57·418	0·204	5300
5400	68·525		48174		58885		57·622		5400
5500									5500
5600									5600
5700									5700
5800									5800
5900									5900
6000									6000

CARBON MONOXIDE

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
100									100
200									200
300									300
400	45·290	1·544	1985	497	2780	695	38·340	1·544	400
500	46·834	1·269	2482	499	3475	698	39·884	1·265	500
600	48·103	1·079	2981	501	4173	699	41·149	1·073	600
700	49·182	0·936	3482	504	4872	703	42·222	0·927	700
800	50·118	0·830	3986	507	5575	706	43·149	0·819	800
900	50·948	0·753	4493	517	6281	716	43·968	0·736	900
1000	51·701	0·691	5010	527	6997	726	44·704	0·667	1000
1100	52·392	0·639	5537	537	7723	735	45·371	0·611	1100
1200	53·031	0·596	6074	546	8458	745	45·982	0·566	1200
1300	53·627	0·559	6620	556	9203	755	46·548	0·525	1300
1400	54·186	0·526	7176	565	9958	763	47·073	0·492	1400
1500	54·712	0·499	7741	574	10721	773	47·565	0·463	1500
1600	55·211	0·473	8315	582	11494	781	48·028	0·436	1600
1700	55·684	0·451	8897	591	12275	789	48·464	0·414	1700
1800	56·135	0·431	9488	599	13064	798	48·878	0·392	1800
1900	56·566	0·412	10087	605	13862	804	49·270	0·375	1900
2000	56·978	0·396	10692	612	14666	810	49·645	0·359	2000
2100	57·374	0·379	11304	618	15476	817	50·004	0·344	2100
2200	57·753	0·366	11922	624	16293	823	50·348	0·329	2200
2300	58·119	0·352	12546	629	17116	827	50·677	0·318	2300
2400	58·471	0·340	13175	635	17943	834	50·995	0·305	2400
2500	58·811	0·328	13810	638	18777	837	51·300	0·296	2500
2600	59·139	0·317	14448	642	19614	841	51·596	0·284	2600
2700	59·456	0·307	15090	645	20455	843	51·880	0·276	2700
2800	59·763	0·297	15735	649	21298	848	52·156	0·268	2800
2900	60·060	0·288	16384	653	22146	852	52·424	0·258	2900
3000	60·348	0·280	17037	656	22998	854	52·682	0·252	3000
3100	60·628	0·273	17693	658	23852	857	52·934	0·245	3100
3200	60·901	0·264	18351	660	24709	859	53·179	0·238	3200
3300	61·165	0·257	19011	662	25568	860	53·417	0·233	3300
3400	61·422	0·250	19673	665	26428	864	53·650	0·223	3400
3500	61·672	0·244	20338	668	27292	867	53·873	0·222	3500
3600	61·916	0·238	21006	669	28159	867	54·095	0·214	3600
3700	62·154	0·231	21675	671	29026	870	54·309	0·209	3700
3800	62·385	0·227	22346	673	29896	872	54·518	0·205	3800
3900	62·612	0·221	23019	674	30768	873	54·723	0·200	3900
4000	62·833	0·216	23693	676	31641	874	54·923	0·195	4000
4100	63·049	0·210	24369	677	32515	876	55·118	0·192	4100
4200	63·259	0·207	25046	679	33391	878	55·310	0·187	4200
4300	63·466	0·202	25725	680	34269	878	55·497	0·182	4300
4400	63·668	0·198	26405	682	35147	881	55·679	0·180	4400
4500	63·866	0·194	27087	684	36028	882	55·859	0·177	4500

CARBON MONOXIDE (*continued*)

T° F. Abs.	S		E		H		$-\frac{F}{T}$		T° F. Abs.
4600	64·060	0·189	27771	684	36910	883	56·036	0·173	4600
4700	64·249	0·186	28455	685	37793	884	56·209	0·167	4700
4800	64·435	0·183	29140	687	38677	886	56·376	0·167	4800
4900	64·618	0·179	29827	687	39563	886	56·543	0·164	4900
5000	64·797	0·176	30514	688	40449	886	56·707	0·161	5000
5100	64·973	0·172	31202	689	41335	887	56·868	0·158	5100
5200	65·145	0·169	31891	690	42222	889	57·026	0·154	5200
5300	65·314	0·166	32581	690	43111	889	57·180	0·153	5300
5400	65·480	0·163	33271	691	44000	890	57·333	0·149	5400
5500	65·643	0·160	33962	691	44890	890	57·482	0·146	5500
5600	65·803	0·158	34653	692	45780	891	57·628	0·145	5600
5700	65·961	0·155	35345	693	46671	891	57·773	0·142	5700
5800	66·116	0·153	36038	693	47562	892	57·915	0·141	5800
5900	66·269	0·150	36731	694	48454	892	58·056	0·139	5900
6000	66·419	0·148	37425	695	49346	894	58·195	0·136	6000
6100	66·567	0·146	38120	696	50240	895	58·331	0·134	6100
6200	66·713	0·143	38816	698	51135	896	58·465	0·132	6200
6300	66·856	0·141	39514	698	52031	897	58·597	0·130	6300
6400	66·997	0·139	40212	699	52928	898	58·727	0·130	6400
6500	67·136	0·137	40911	699	53826	898	58·857	0·126	6500
6600	67·273	0·135	41610	700	54724	899	58·983	0·125	6600
6700	67·408	0·133	42310	701	55623	899	59·108	0·123	6700
6800	67·541	0·132	43011	701	56522	899	59·231	0·121	6800
6900	67·673	0·130	43712	702	57421	900	59·352	0·121	6900
7000	67·803	0·128	44414	702	58321	901	59·473	0·119	7000
7100	67·931	0·126	45116	702	59222	901	59·592	0·115	7100
7200	68·057	0·124	45818	702	60123	901	59·707	0·115	7200
7300	68·181	0·123	46520	702	61024	901	59·822	0·114	7300
7400	68·304	0·121	47222	702	61925	901	59·936	0·112	7400
7500	68·425	0·119	47924	703	62826	902	60·048	0·112	7500
7600	68·544	0·118	48627	704	63728	902	60·160	0·110	7600
7700	68·662	0·117	49331	704	64630	903	60·270	0·109	7700
7800	68·779	0·115	50035	704	65533	903	60·379	0·108	7800
7900	68·894	0·114	50739	706	66436	904	60·487	0·105	7900
8000	69·008	0·112	51445	706	67340	905	60·592	0·104	8000
8100	69·120	0·111	52151	707	68245	906	60·696	0·104	8100
8200	69·231	0·110	52858	709	69151	907	60·800	0·102	8200
8300	69·341	0·109	53567	709	70058	908	60·902	0·101	8300
8400	69·450	0·108	54276	710	70966	909	61·003	0·101	8400
8500	69·558	0·106	54986	711	71875	909	61·104	0·100	8500
8600	69·664	0·105	55697	711	72784	910	61·204	0·097	8600
8700	69·769	0·104	56408	711	73694	910	61·301	0·096	8700
8800	69·873	0·103	57119	712	74604	910	61·397	0·094	8800
8900	69·976	0·101	57831	713	75514	910	61·491	0·094	8900
9000	70·077		58544		76424		61·585		9000

HYDROGEN

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
100									100
200									200
300									300
400	29·249	1·504	1916	479	2711	677	22·473	1·505	400
500	30·753	1·256	2395	492	3388	691	23·978	1·233	500
600	32·009	1·069	2887	496	4079	694	25·211	1·050	600
700	33·078	0·928	3383	498	4773	697	26·261	0·908	700
800	34·006	0·822	3881	500	5470	699	27·169	0·804	800
900	34·828	0·736	4381	501	6169	700	27·973	0·722	900
1000	35·564	0·668	4882	502	6869	701	28·695	0·655	1000
1100	36·232	0·610	5384	504	7570	702	29·350	0·598	1100
1200	36·842	0·564	5888	506	8272	705	29·948	0·553	1200
1300	37·406	0·523	6394	508	8977	707	30·501	0·511	1300
1400	37·929	0·489	6902	510	9684	708	31·012	0·478	1400
1500	38·418	0·458	7412	513	10392	712	31·490	0·446	1500
1600	38·876	0·434	7925	516	11104	715	31·936	0·422	1600
1700	39·310	0·411	8441	521	11819	719	32·358	0·398	1700
1800	39·721	0·392	8962	526	12538	725	32·756	0·377	1800
1900	40·113	0·375	9488	532	13263	731	33·133	0·358	1900
2000	40·488	0·359	10020	538	13994	736	33·491	0·342	2000
2100	40·847	0·344	10558	542	14730	741	33·833	0·326	2100
2200	41·191	0·331	11100	547	15471	746	34·159	0·312	2200
2300	41·522	0·319	11647	550	16217	748	34·471	0·301	2300
2400	41·841	0·309	12197	556	16965	755	34·772	0·290	2400
2500	42·150	0·299	12753	564	17720	763	35·062	0·278	2500
2600	42·449	0·290	13317	570	18483	769	35·340	0·268	2600
2700	42·739	0·282	13887	577	19252	778	35·608	0·259	2700
2800	43·021	0·274	14464	582	20030	778	35·867	0·253	2800
2900	43·295	0·267	15046	587	20808	786	36·120	0·244	2900
3000	43·562	0·259	15633	592	21594	790	36·364	0·236	3000
3100	43·821	0·253	16225	598	22384	797	36·600	0·230	3100
3200	44·074	0·247	16823	603	23181	802	36·830	0·223	3200
3300	44·321	0·240	17426	607	23983	805	37·053	0·218	3300
3400	44·561	0·235	18033	612	24788	811	37·271	0·210	3400
3500	44·796	0·230	18645	618	25599	817	37·481	0·208	3500
3600	45·026	0·225	19263	622	26416	820	37·689	0·201	3600
3700	45·251	0·220	19885	627	27236	826	37·890	0·197	3700
3800	45·471	0·216	20512	631	28062	830	38·087	0·192	3800
3900	45·687	0·211	21143	635	28892	834	38·279	0·188	3900
4000	45·898	0·206	21778	638	29726	836	38·467	0·182	4000
4100	46·104	0·203	22416	642	30562	841	38·649	0·182	4100
4200	46·307	0·198	23058	646	31403	845	38·831	0·175	4200
4300	46·505	0·195	23704	649	32248	847	39·006	0·172	4300
4400	46·700	0·191	24353	653	33095	852	39·178	0·169	4400
4500	46·891	0·188	25006	656	33947	855	39·347	0·166	4500

HYDROGEN (*continued*)

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
4600	47·079	0·185	25662	660	34802	858	39·513	0·165	4600
4700	47·264	0·181	26322	663	35660	862	39·678	0·158	4700
4800	47·445	0·179	26985	666	36522	865	39·836	0·158	4800
4900	47·624	0·175	27651	668	37387	867	39·994	0·154	4900
5000	47·799	0·172	28319	672	38254	870	40·148	0·152	5000
5100	47·971	0·170	28991	674	39124	873	40·300	0·150	5100
5200	48·141	0·166	29665	677	39997	876	40·450	0·145	5200
5300	48·307	0·164	30342	679	40873	877	40·595	0·146	5300
5400	48·471	0·161	31021	680	41750	879	40·741	0·141	5400
5500	48·632	0·159	31701	682	42629	881	40·882	0·140	5500
5600	48·791	0·156	32383	685	43510	883	41·022	0·137	5600
5700	48·947	0·153	33068	688	44393	887	41·159	0·135	5700
5800	49·100	0·152	33756	691	45280	890	41·291	0·134	5800
5900	49·252	0·151	34447	694	46170	892	41·428	0·132	5900
6000	49·403	0·148	35141	695	47062	894	41·560	0·129	6000
6100	49·551	0·147	35836	697	47956	896	41·689	0·128	6100
6200	49·698	0·143	36533	701	48852	899	41·817	0·127	6200
6300	49·841	0·141	37234	702	49751	901	41·944	0·125	6300
6400	49·982	0·140	37936	703	50652	902	42·069	0·123	6400
6500	50·122	0·138	38639	705	51554	904	42·192	0·122	6500
6600	50·260	0·137	39344	708	52458	906	42·314	0·120	6600
6700	50·397	0·136	40052	709	53364	908	42·434	0·119	6700
6800	50·533	0·134	40761	711	54272	910	42·553	0·117	6800
6900	50·667	0·131	41472	714	55182	912	42·670	0·115	6900
7000	50·798	0·129	42186	715	56094	914	42·785	0·113	7000
7100	50·927	0·127	42901	717	57008	916	42·898	0·111	7100
7200	51·054	0·126	43618	719	57924	917	43·009	0·110	7200
7300	51·180	0·125	44337	719	58841	918	43·119	0·110	7300
7400	51·305	0·123	45056	721	59759	920	43·229	0·108	7400
7500	51·428	0·121	45777	723	60679	921	43·337	0·107	7500
7600	51·549	0·121	46500	724	61600	923	43·444	0·106	7600
7700	51·670	0·120	47224	725	62523	924	43·550	0·105	7700
7800	51·790	0·118	47949	726	63447	925	43·655	0·104	7800
7900	51·908	0·117	48675	728	64372	926	43·759	0·103	7900
8000	52·025	0·115	49403	729	65298	928	43·862	0·102	8000
8100	52·140	0·114	50132	730	66226	929	43·964	0·101	8100
8200	52·254	0·113	50862	732	67155	930	44·065	0·100	8200
8300	52·367	0·112	51594	732	68085	931	44·165	0·098	8300
8400	52·479	0·110	52326	734	69016	933	44·263	0·097	8400
8500	52·589	0·109	53060	737	69949	935	44·360	0·096	8500
8600	52·698	0·108	53797	737	70884	936	44·456	0·095	8600
8700	52·806	0·107	54534	739	71820	938	44·551	0·094	8700
8800	52·913	0·106	55273	741	72758	939	44·645	0·094	8800
8900	53·019	0·106	56014	741	73697	940	44·739	0·093	8900
9000	53·125		56755		74637		44·832		9000

HYDROXYL (OH)

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
100									100
200									200
300									300
400									400
500									500
600	44·711	1·097	3060	506	4252	704	37·625	1·103	600
700	45·808	0·933	3566	505	4956	704	38·728	0·938	700
800	46·741	0·828	4071	503	5660	702	39·666	0·834	800
900	47·569	0·745	4574	509	6362	708	40·500	0·744	900
1000	48·314	0·676	5083	509	7070	708	41·244	0·675	1000
1100	48·990	0·613	5592	510	7778	708	41·919	0·612	1100
1200	49·603	0·574	6102	511	8486	710	42·531	0·572	1200
1300	50·177	0·527	6613	511	9196	710	43·103	0·525	1300
1400	50·704	0·485	7124	515	9906	713	43·628	0·482	1400
1500	51·189	0·461	7639	516	10619	715	44·110	0·456	1500
1600	51·650	0·439	8155	525	11334	724	44·566	0·430	1600
1700	52·089	0·419	8680	535	12058	733	44·996	0·406	1700
1800	52·508	0·402	9215	544	12791	743	45·402	0·385	1800
1900	52·910	0·382	9759	547	13534	746	45·787	0·365	1900
2000	53·292	0·366	10306	552	14280	750	46·152	0·349	2000
2100	53·658	0·352	10858	556	15030	755	46·501	0·334	2100
2200	54·010	0·339	11414	562	15785	761	46·835	0·320	2200
2300	54·349	0·323	11976	567	16546	765	47·155	0·304	2300
2400	54·672	0·313	12543	573	17311	772	47·459	0·293	2400
2500	54·985	0·305	13116	576	18083	775	47·752	0·285	2500
2600	55·290	0·296	13692	583	18858	782	48·037	0·275	2600
2700	55·586	0·286	14275	591	19640	789	48·312	0·264	2700
2800	55·872	0·282	14866	597	20429	796	48·576	0·259	2800
2900	56·154	0·272	15463	602	21225	801	48·835	0·249	2900
3000	54·426	0·263	16065	611	22026	809	49·084	0·239	3000
3100	56·689	0·256	16676	614	22835	813	49·323	0·232	3100
3200	56·945	0·251	17290	619	23648	818	49·555	0·227	3200
3300	57·196	0·248	17909	622	24466	820	49·782	0·225	3300
3400	57·444	0·239	18531	625	25286	824	50·007	0·216	3400
3500	57·683	0·232	19156	630	26110	829	50·223	0·209	3500
3600	57·915	0·230	19786	632	26939	830	50·432	0·208	3600
3700	58·145	0·225	20418	635	27769	834	50·640	0·203	3700
3800	58·370	0·218	21053	639	28603	838	50·843	0·196	3800
3900	58·588	0·211	21692	643	29441	842	51·039	0·189	3900
4000	58·799	0·208	22335	648	30283	846	51·228	0·186	4000
4100	59·007	0·204	22983	652	31129	851	51·414	0·182	4100
4200	59·211	0·202	23635	658	31980	857	51·596	0·180	4200
4300	59·413	0·198	24293	663	32837	861	51·776	0·176	4300
4400	59·611	0·192	24956	663	33698	862	51·952	0·171	4400
4500	59·803	0·189	25619	665	34560	864	52·123	0·168	4500

HYDROXYL (*continued*)

$T°$ F. Abs.	S		E		H		$-\frac{F}{T}$		$T°$ F. Abs.
4600	59·992	0·188	26284	671	35424	869	52·291	0·167	4600
4700	60·180	0·185	26955	674	36293	873	52·458	0·164	4700
4800	60·365	0·182	27629	675	37166	874	52·622	0·161	4800
4900	60·547	0·177	28304	676	38040	875	52·783	0·157	4900
5000	60·724	0·173	28980	678	38915	876	52·940	0·154	5000
5100	60·897	0·169	29658	678	39791	877	53·094	0·151	5100
5200	61·066	0·167	30336	678	40668	877	53·245	0·149	5200
5300	61·233	0·163	31014	678	41545	877	53·394	0·146	5300
5400	61·396	0·162	31692	679	42422	877	53·540	0·145	5400
5500	61·558	0·158	32371	680	43299	879	53·685	0·142	5500
5600	61·716	0·156	33051	683	44178	881	53·827	0·140	5600
5700	61·872	0·154	33734	684	45059	883	53·967	0·138	5700
5800	62·026	0·152	34418	687	45942	886	54·105	0·136	5800
5900	62·178	0·149	35105	692	46828	890	54·241	0·133	5900
6000	62·327	0·148	35797	694	47718	893	54·374	0·132	6000
6100	62·475	0·146	36491	697	48611	896	54·506	0·130	6100
6200	62·621	0·142	37188	701	49507	899	54·636	0·126	6200
6300	62·763	0·141	37889	704	50406	903	54·762	0·125	6300
6400	62·904	0·140	38593	707	51309	906	54·887	0·124	6400
6500	64·014	0·139	39300	709	52215	908	55·011	0·123	6500
6600	63·183	0·138	40009	715	53123	913	55·134	0·122	6600
6700	63·321	0·137	40724	716	54036	915	55·256	0·121	6700
6800	63·458	0·136	41440	719	54951	918	55·377	0·120	6800
6900	63·594	0·134	42159	724	55869	922	55·497	0·118	6900
7000	63·728	0·132	42883	726	56791	925	55·615	0·116	7000
7100	63·860	0·129	43609	729	57716	928	55·731	0·113	7100
7200	63·989	0·128	44338	731	58644	929	55·844	0·112	7200
7300	64·117	0·127	45069	731	59573	930	55·956	0·111	7300
7400	64·244	0·125	45800	732	60503	931	56·067	0·109	7400
7500	64·369	0·124	46532	733	61434	932	56·176	0·108	7500
7600	64·493	0·122	47265	734	62366	932	56·284	0·107	7600
7700	64·615	0·121	47999	735	63298	934	56·391	0·106	7700
7800	64·736	0·119	48734	735	64232	934	56·497	0·105	7800
7900	64·855	0·118	49469	736	65166	934	56·602	0·104	7900
8000	64·973	0·117	50205	736	66100	935	56·706	0·103	8000
8100	65·090	0·115	50941	737	67035	936	56·809	0·102	8100
8200	65·205	0·113	51678	738	67971	936	56·911	0·101	8200
8300	65·318	0·112	52416	738	68907	937	57·012	0·100	8300
8400	65·430	0·111	53154	739	69844	938	57·112	0·099	8400
8500	65·541	0·110	53893	740	70782	939	57·211	0·098	8500
8600	65·651	0·108	54633	741	71721	939	57·309	0·096	8600
8700	65·759	0·106	55374	741	72660	940	57·405	0·095	8700
8800	65·865	0·105	56115	743	73600	941	57·500	0·094	8800
8900	65·970	0·104	56858	743	74541	942	57·594	0·093	8900
9000	66·074		57601		75483		57·687		9000

NITRIC OXIDE (NO)

T° F. Abs.	S		E		H		$-\frac{F}{T}$		T° F. Abs.
100									100
200									200
300									300
400									400
500									500
600	51·142	1·110	3213	516	4405	714	43·801	1·138	600
700	52·252	0·954	3729	520	5119	719	44·939	0·969	700
800	53·206	0·856	4249	527	5838	726	45·908	0·861	800
900	54·062	0·773	4776	535	6564	734	46·769	0·768	900
1000	54·835	0·710	5311	542	7298	741	47·537	0·700	1000
1100	55·545	0·650	5853	549	8039	747	48·237	0·636	1100
1200	56·195	0·598	6402	560	8786	759	48·873	0·578	1200
1300	56·793	0·581	6962	571	9545	770	49·451	0·555	1300
1400	57·374	0·543	7533	587	10315	785	50·006	0·511	1400
1500	57·917	0·516	8120	600	11100	799	50·517	0·479	1500
1600	58·433	0·488	8720	610	11899	809	50·996	0·450	1600
1700	58·921	0·471	9330	619	12708	817	51·446	0·432	1700
1800	59·392	0·441	9949	621	13525	820	51·878	0·406	1800
1900	59·833	0·422	10570	629	14345	828	52·284	0·389	1900
2000	60·255	0·397	11199	638	15173	836	52·673	0·369	2000
2100	60·652	0·393	11837	642	16009	841	53·042	0·358	2100
2200	61·045	0·381	12479	647	16850	846	53·400	0·339	2200
2300	61·426	0·366	13126	653	17696	851	53·739	0·327	2300
2400	61·792	0·348	13779	654	18547	853	54·066	0·314	2400
2500	62·140	0·333	14433	655	19400	854	54·380	0·304	2500
2600	62·473	0·324	15088	656	20254	855	54·684	0·295	2600
2700	62·797	0·308	15744	657	21109	856	54·979	0·284	2700
2800	63·105	0·299	16401	658	21965	856	55·263	0·274	2800
2900	63·404	0·288	17059	658	22821	857	55·537	0·267	2900
3000	63·692	0·282	17717	661	23678	859	55·804	0·259	3000
3100	63·974	0·273	18378	662	24537	861	56·063	0·252	3100
3200	64·247	0·264	19040	664	25398	863	56·315	0·245	3200
3300	64·511	0·259	19704	669	26261	867	56·560	0·237	3300
3400	64·770	0·256	20373	671	27128	870	56·797	0·231	3400
3500	65·026	0·249	21044	675	27998	874	57·028	0·227	3500
3600	65·275	0·241	21719	679	28872	877	57·255	0·221	3600
3700	65·516	0·236	22398	680	29749	879	57·476	0·214	3700
3800	65·752	0·231	23078	683	30628	882	57·690	0·211	3800
3900	65·983	0·223	23761	685	31510	884	57·901	0·205	3900
4000	66·206	0·219	24446	688	32394	886	58·106	0·200	4000
4100	66·425	0·213	25134	689	33280	888	58·306	0·195	4100
4200	66·638	0·207	25823	689	34168	888	58·501	0·191	4200
4300	66·845	0·204	26512	690	35056	888	58·692	0·188	4300
4400	67·049	0·199	27202	690	35944	889	58·880	0·183	4400
4500	67·248	0·195	27892	690	36833	889	59·063	0·181	4500

NITRIC OXIDE (*continued*)

T° F. Abs.	S		E		H		$-\frac{F}{T}$		T° F. Abs.
4600	67·443	0·191	28582	692	37722	890	59·244	0·176	4600
4700	67·634	0·188	29274	692	38612	891	59·420	0·173	4700
4800	67·822	0·183	29966	692	39503	891	59·593	0·170	4800
4900	68·005	0·181	30658	693	40394	892	59·763	0·167	4900
5000	68·186	0·177	31351	696	41286	894	59·930	0·163	5000
5100	68·363	0·174	32047	697	42180	896	60·093	0·160	5100
5200	68·537	0·171	32744	699	43076	898	60·253	0·158	5200
5300	68·708	0·169	33443	702	43974	900	60·411	0·156	5300
5400	68·877	0·164	34145	702	44874	901	60·567	0·153	5400
5500	69·041	0·163	34847	702	45775	901	60·720	0·151	5500
5600	69·204	0·161	35549	702	46676	901	60·871	0·148	5600
5700	69·365	0·157	36251	702	47577	901	61·019	0·145	5700
5800	69·522	0·153	36953	702	48478	901	61·164	0·143	5800
5900	69·675	0·152	37655	702	49379	901	61·307	0·141	5900
6000	69·827	0·149	38357	702	50280	901	61·448	0·139	6000
6100	69·976	0·147	39059	703	51181	901	61·587	0·137	6100
6200	70·123	0·147	39762	703	52082	901	61·724	0·136	6200
6300	70·270	0·146	40465	703	52983	901	61·860	0·136	6300
6400	70·416	0·141	41168	704	53884	903	61·996	0·131	6400
6500	70·557	0·137	41872	706	54787	905	62·127	0·127	6500
6600	70·694	0·135	42578	708	55692	906	62·254	0·125	6600
6700	70·829	0·133	43286	708	56598	907	62·379	0·124	6700
6800	70·962	0·132	43994	709	57505	908	62·503	0·123	6800
6900	71·094	0·130	44703	711	58413	909	62·626	0·122	6900
7000	71·224	0·130	45414	712	59322	911	62·748	0·120	7000
7100	71·354	0·127	46126	713	60233	912	62·868	0·118	7100
7200	71·481	0·124	46839	715	61145	913	62·986	0·117	7200
7300	71·605	0·124	47554	715	62058	914	63·103	0·115	7300
7400	71·729	0·122	48269	717	62972	916	63·218	0·114	7400
7500	71·851	0·122	48986	718	63888	916	63·332	0·113	7500
7600	71·973	0·119	49704	719	64804	918	63·445	0·111	7600
7700	72·092	0·118	50423	720	65722	919	63·556	0·110	7700
7800	72·210	0·116	51143	720	66641	919	63·666	0·108	7800
7900	72·326	0·115	51863	722	67560	920	63·774	0·107	7900
8000	72·441	0·114	52585	722	68480	921	63·881	0·106	8000
8100	72·555	0·113	53307	723	69401	922	63·987	0·105	8100
8200	72·668	0·111	54030	724	70323	922	64·092	0·103	8200
8300	72·779	0·110	54754	724	71245	923	64·195	0·102	8300
8400	72·889	0·109	55478	725	72168	924	64·297	0·101	8400
8500	72·998	0·108	56203	728	73092	926	64·398	0·100	8500
8600	73·106	0·106	56931	728	74018	927	64·408	0·099	8600
8700	73·212	0·105	57659	730	74945	929	64·597	0·098	8700
8800	73·317	0·105	58389	735	75874	933	64·695	0·097	8800
8900	73·422	0·104	59124	736	76807	935	64·702	0·096	8900
9000	73·526		59860		77742		64·888		9000

EQUILIBRIUM CONSTANTS

	$K_p = \dfrac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}}$		$K_p = \dfrac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}}$		$K_p = \dfrac{p_{H_2O} \cdot p_{CO}}{p_{H_2} \cdot p_{CO_2}}$		
	$CO + \frac{1}{2}O_2 = CO_2$		$H_2 + \frac{1}{2}O_2 = H_2O$		$CO_2 + H_2 = CO + H_2O$		
T° F. Abs.	$\text{Log}_{10} K_p$	K_p	$\text{Log}_{10} K_p$	K_p	$\text{Log}_{10} K_p$	K_p	T° F. Abs.
600	39·80	$6{\cdot}3096 \times 10^{39}$	35·840	$6{\cdot}918 \times 10^{35}$	−4·231	$5{\cdot}875 \times 10^{-5}$	600
700	33·46	$2{\cdot}8840 \times 10^{33}$	30·141	$1{\cdot}384 \times 10^{30}$	−3·318	$4{\cdot}808 \times 10^{-4}$	700
800	28·70	$5{\cdot}0119 \times 10^{28}$	25·972	$9{\cdot}370 \times 10^{25}$	−2·638	$2{\cdot}301 \times 10^{-3}$	800
900	25·00	1×10^{25}	22·882	$7{\cdot}621 \times 10^{22}$	−2·115	$7{\cdot}674 \times 10^{-3}$	900
1000	22·04	$1{\cdot}0965 \times 10^{22}$	20·333	$2{\cdot}153 \times 10^{20}$	−1·703	$1{\cdot}982 \times 10^{-2}$	1000
1100	19·61	$4{\cdot}0738 \times 10^{19}$	18·242	$1{\cdot}746 \times 10^{18}$	−1·370	$4{\cdot}266 \times 10^{-2}$	1100
1200	17·59	$3{\cdot}8905 \times 10^{17}$	16·497	$3{\cdot}141 \times 10^{16}$	−1·096	$8{\cdot}017 \times 10^{-2}$	1200
1300	15·89	$7{\cdot}7625 \times 10^{15}$	15·017	$1{\cdot}040 \times 10^{15}$	−0·8673	0·1357	1300
1400	14·42	$2{\cdot}6303 \times 10^{14}$	13·747	$5{\cdot}585 \times 10^{13}$	−0·6745	0·2116	1400
1500	13·15	$1{\cdot}4125 \times 10^{13}$	12·643	$4{\cdot}395 \times 10^{12}$	−0·5099	0·3091	1500
1600	12·04	$1{\cdot}0965 \times 10^{12}$	11·676	$4{\cdot}742 \times 10^{11}$	−0·3683	0·4283	1600
1700	11·07	$1{\cdot}1749 \times 10^{11}$	10·821	$6{\cdot}622 \times 10^{10}$	−0·2459	0·5677	1700
1800	10·20	$1{\cdot}5849 \times 10^{10}$	10·061	$1{\cdot}151 \times 10^{10}$	−0·1384	0·7271	1800
1900	9·423	$2{\cdot}6485 \times 10^{9}$	9·379	$2{\cdot}393 \times 10^{9}$	−0·0435	0·9047	1900
2000	8·724	$5{\cdot}2966 \times 10^{8}$	8·765	$5{\cdot}821 \times 10^{8}$	0·0407	1·098	2000
2100	8·093	$1{\cdot}2388 \times 10^{8}$	8·208	$1{\cdot}614 \times 10^{8}$	0·1154	1·304	2100
2200	7·519	$3{\cdot}3037 \times 10^{7}$	7·701	$5{\cdot}023 \times 10^{7}$	0·1825	1·522	2200
2300	6·996	$9{\cdot}9083 \times 10^{6}$	7·238	$1{\cdot}730 \times 10^{7}$	0·2426	1·748	2300
2400	6·517	$3{\cdot}2885 \times 10^{6}$	6·814	$6{\cdot}516 \times 10^{6}$	0·2971	1·982	2400
2500	6·077	$1{\cdot}1940 \times 10^{6}$	6·422	$2{\cdot}642 \times 10^{6}$	0·3460	2·218	2500
2600	5·670	$4{\cdot}6774 \times 10^{5}$	6·061	$1{\cdot}151 \times 10^{6}$	0·3908	2·459	2600
2700	5·295	$1{\cdot}9724 \times 10^{5}$	5·726	$5{\cdot}321 \times 10^{5}$	0·4313	2·700	2700
2800	4·946	$8{\cdot}8308 \times 10^{4}$	5·415	$2{\cdot}600 \times 10^{5}$	0·4689	2·944	2800
2900	4·622	$4{\cdot}1879 \times 10^{4}$	5·125	$1{\cdot}333 \times 10^{5}$	0·5027	3·182	2900
3000	4·320	$2{\cdot}0893 \times 10^{4}$	4·854	$7{\cdot}145 \times 10^{4}$	0·5336	3·417	3000

EQUILIBRIUM CONSTANTS (*continued*)

$T°$ F. Abs.	$K_p = \dfrac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}}$ $CO + \frac{1}{2}O_2 = CO_2$		$K_p = \dfrac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}}$ $H_2 + \frac{1}{2}O_2 = H_2O$		$K_p = \dfrac{p_{H_2O} \cdot p_{CO}}{p_{H_2} \cdot p_{CO_2}}$ $CO_2 + H_2 = CO + H_2O$		$T°$ F. Abs.
	$\mathrm{Log}_{10} K_p$	K_p	$\mathrm{Log}_{10} K_p$	K_p	$\mathrm{Log}_{10} K_p$	K_p	
3100	4·037	$1·0889 \times 10^4$	4·600	$3·981 \times 10^4$	0·5624	3·651	3100
3200	3·773	$5·9293 \times 10^3$	4·363	$2·307 \times 10^4$	0·5893	3·884	3200
3300	3·525	$3·3497 \times 10^3$	4·139	$1·377 \times 10^4$	0·6140	4·112	3300
3400	3·291	$1·9543 \times 10^3$	3·929	8492	0·6372	4·337	3400
3500	3·072	$1·1803 \times 10^3$	3·730	5370	0·6579	4·549	3500
3600	2·865	732·82	3·543	3491	0·6776	4·760	3600
3700	2·668	465·59	3·365	2317	0·6962	4·968	3700
3800	2·483	304·09	3·197	1574	0·7132	5·167	3800
3900	2·307	202·77	3·037	1089	0·7296	5·365	3900
4000	2·141	138·36	2·885	767·4	0·7447	5·555	4000
4100	1·982	95·940	2·741	550·8	0·7593	5·745	4100
4200	1·832	67·920	2·604	401·8	0·7722	5·918	4200
4300	1·688	48·753	2·473	297·2	0·7847	6·091	4300
4400	1·551	35·563	2·345	221·3	0·7963	6·256	4400
4500	1·420	26·303	2·228	169·0	0·8077	6·422	4500
4600	1·295	19·724	2·113	129·7	0·8179	6·575	4600
4700	1·176	14·997	2·004	100·9	0·8273	6·719	4700
4800	1·062	11·535	1·898	79·07	0·8365	6·863	4800
4900	0·9521	8·9557	1·797	62·66	0·8452	7·002	4900
5000	0·8467	7·0259	1·701	50·23	0·8538	7·142	5000
5100	0·7459	5·5705	1·608	40·55	0·8616	7·271	5100
5200	0·6491	4·4576	1·518	32·96	0·8691	7·398	5200
5300	0·5561	3·5983	1·432	27·04	0·8763	7·521	5300
5400	0·4667	2·9289	1·349	22·34	0·8824	7·628	5400

EQUILIBRIUM CONSTANTS FOR THE REACTION $\frac{1}{2}H_2 + OH \rightleftharpoons H_2O$; $\Delta E_0 = -120420$ B.Th.U./lb. mol

$$K_p = \frac{p_{H_2O}}{p_{OH} \cdot p_{H_2}^{\frac{1}{2}}}.$$

$T°$ F. Abs.	$\text{Log}_{10} K_p$	K_p	$T°$ F. Abs.	$\text{Log}_{10} K_p$	K_p
600	41·204	$1·560 \times 10^{41}$	3100	5·0638	$1·152 \times 10^5$
700	34·851	$7·096 \times 10^{34}$	3200	4·7895	$6·159 \times 10^4$
800	30·080	$1·202 \times 10^{30}$	3300	4·5314	$3·400 \times 10^4$
900	26·361	$2·296 \times 10^{26}$	3400	4·2877	$1·940 \times 10^4$
1000	23·381	$2·404 \times 10^{23}$	3500	4·0566	$1·139 \times 10^4$
1100	20·939	$8·690 \times 10^{20}$	3600	3·8407	$6·930 \times 10^3$
1200	18·901	$7·962 \times 10^{18}$	3700	3·6361	4326
1300	17·173	$1·489 \times 10^{17}$	3800	3·4413	2763
1400	15·691	$4·909 \times 10^{15}$	3900	3·2571	1808
1500	14·406	$2·547 \times 10^{14}$	4000	3·0826	1210
1600	13·379	$2·393 \times 10^{13}$	4100	2·9108	814·3
1700	12·284	$1·923 \times 10^{12}$	4200	2·7585	573·5
1800	11·399	$2·506 \times 10^{11}$	4300	2·6070	404·6
1900	10·606	$4·037 \times 10^{10}$	4400	2·4623	289·9
2000	9·8920	$7·798 \times 10^9$	4500	2·3250	211·4
2100	9·2454	$1·760 \times 10^9$	4600	2·1930	156·0
2200	8·6573	$4·543 \times 10^8$	4700	2·0669	116·7
2300	8·1196	$1·317 \times 10^8$	4800	1·9451	88·12
2400	7·6276	$4·242 \times 10^7$	4900	1·8289	67·44
2500	7·1742	$1·494 \times 10^7$	5000	1·7176	52·19
2600	6·7555	$5·695 \times 10^6$	5100	1·6109	40·82
2700	6·3668	$2·327 \times 10^6$	5200	1·5082	32·23
2800	6·0066	$1·014 \times 10^6$	5300	1·4094	25·67
2900	5·6704	$4·682 \times 10^5$	5400	1·3140	20·61
3000	5·3563	$2·272 \times 10^5$			

LOWER HEATS OF REACTION

$CO+\frac{1}{2}O_2=CO_2$; $\Delta E_0=-120163$ B.Th.U./lb. mol

T° F. Abs.	H_v		H_p		T° F. Abs.	H_v		H_p	
400	121041	105	121438	205	3400	116329	230	119706	130
500	121146	52	121643	151	3500	116099	231	119576	132
600	121198	8	121794	107	3600	115868	232	119444	133
700	121206	37	121901	63	3700	115636	232	119311	133
800	121169	71	121964	28	3800	115404	233	119178	133
900	121098	95	121992	5	3900	115171	234	119045	134
1000	121003	106	121997	7	4000	114937	234	118911	135
1100	120897	133	121990	34	4100	114703	234	118776	135
1200	120764	142	121956	42	4200	114469	235	118641	135
1300	120622	153	121914	54	4300	114234	235	118506	136
1400	120469	163	121860	64	4400	113999	236	118370	137
1500	120306	172	121796	73	4500	113763	236	118233	137
1600	120134	180	121723	80	4600	113527	237	118096	137
1700	119954	186	121643	87	4700	113290	237	117959	138
1800	119768	191	121556	92	4800	113053	237	117821	138
1900	119577	198	121464	98	4900	112816	238	117683	138
2000	119379	201	121366	102	5000	112578	238	117545	139
2100	119178	204	121264	105	5100	112340	239	117406	139
2200	118974	208	121159	108	5200	112101	239	117267	140
2300	118766	210	121051	111	5300	111862	239	117127	139
2400	118556	213	120940	114	5400	111623	237	116988	138
2500	118343	217	120826	117	5500	111390	235	116850	137
2600	118126	218	120709	119	5600	111155	235	116713	136
2700	117908	222	120590	123	5700	110920	235	116577	135
2800	117686	223	120467	123	5800	110685	235	116442	135
2900	117463	224	120344	125	5900	110450	235	116307	134
3000	117239	226	120219	127	6000	110216	234	116173	134
3100	117013	227	120092	127	6100	109982	233	116039	134
3200	116786	228	119965	129	6200	109749	233	115905	134
3300	116558	229	119836	130	6300	109516		115771	

LOWER HEATS OF REACTION

$H_2 + \frac{1}{2}O_2 = H_2O$; $\Delta E_0 = -102800$ B.Th.U./lb. mol

$T°$ F. Abs.	H_v		H_p		$T°$ F. Abs.	H_v		H_p	
100					3100	104791	41	107871	58
200					3200	104750	44	107929	56
300					3300	104706	52	107985	47
400	103304	121	103702	220	3400	104654	54	108032	45
500	103425	135	103922	234	3500	104600	56	108077	44
600	103560	139	104156	238	3600	104544	58	108121	41
700	103699	136	104394	236	3700	104486	62	108162	37
800	103835	135	104630	235	3800	104424	64	108199	36
900	103970	134	104865	233	3900	104360	65	108235	34
1000	104104	111	105098	210	4000	104295	68	108269	32
1100	104215	108	105308	207	4100	104227	68	108301	31
1200	104323	103	105515	203	4200	104159	71	108332	28
1300	104426	93	105718	192	4300	104088	71	108360	28
1400	104519	84	105910	183	4400	104017	73	108388	27
1500	104603	75	106093	175	4500	103944	75	108415	24
1600	104678	64	106268	163	4600	103869	76	108439	23
1700	104742	55	106431	154	4700	103793	78	108462	22
1800	104797	47	106585	147	4800	103715	78	108484	21
1900	104844	38	106732	137	4900	103637	79	108505	20
2000	104882	28	106869	127	5000	103558	80	108525	20
2100	104910	19	106996	119	5100	103478	80	108545	20
2200	104929	9	107115	108	5200	103398	80	108565	20
2300	104938	1	107223	100	5300	103318	81	108585	16
2400	104939	7	107323	93	5400	103237		108601	
2500	104932	10	107416	89	5500				
2600	104922	14	107505	85	5600				
2700	104908	17	107590	83	5700				
2800	104891	31	107673	67	5800				
2900	104860	32	107740	67	5900				
3000	104828	37	107809	62	6000				

LOWER HEATS OF REACTION

$\frac{1}{2}H_2 + OH \rightarrow H_2O$; $\Delta E_0 = -120420$ B.Th.U./lb. mol

$T°$ F. Abs.	H_v		H_p		$T°$ F. Abs.	H_v		H_p	
600	121318	139	121904	238	3100	121693	71	124772	29
700	121457	130	122142	229	3200	121622	73	124801	26
800	121587	118	122371	218	3300	121549	82	124827	17
900	121705	109	122589	218	3400	121467	85	124844	15
1000	121814	83	122807	183	3500	121382	87	124859	12
1100	121897	80	122990	180	3600	121295	90	124871	9
1200	121977	67	123170	179	3700	121205	95	124880	5
1300	122044	50	123349	138	3800	121110	96	124885	3
1400	122094	39	123487	136	3900	121014	96	124888	3
1500	122133	25	123623	124	4000	120918	97	124891	3
1600	122158	19	123747	119	4100	120821	97	124894	3
1700	122177	14	123866	113	4200	120724	97	124897	2
1800	122191	8	123979	107	4300	120627	98	124899	1
1900	122199	3	124086	97	4400	120529	100	124900	1
2000	122196	14	124183	85	4500	120429	102	124899	3
2100	122182	23	124268	76	4600	120227	104	124896	4
2200	122159	31	124344	69	4700	120223	105	124892	6
2300	122128	38	124413	61	4800	120118	106	124886	6
2400	122090	45	124474	54	4900	120012	109	124880	10
2500	122045	50	124528	50	5000	119903	110	124870	11
2600	121995	55	124578	46	5100	119793	112	124859	12
2700	121940	56	124624	44	5200	119681	114	124847	15
2800	121884	61	124668	36	5300	119576	119	124832	20
2900	121823	65	124704	34	5400	119448		124812	
3000	121758	65	124738	34					

LOWER HEATS OF REACTION

$\frac{1}{2}N_2+\frac{1}{2}O_2 \rightleftarrows NO$; $\Delta E_0=38520$ B.Th.U./lb. mol

T° F. Abs.	$H_v=H_p$		T° F. Abs.	$H_v=H_p$		T° F. Abs.	$H_v=H_p$	
100			3100	38880	6	6100	38440	31
200			3200	38874	6	6200	38409	31
300			3300	38868	7	6300	38378	31
400			3400	38861	7	6400	38347	32
500			3500	38854	7	6500	38315	32
600	38756	3	3600	38847	7	6600	38283	32
700	38759	5	3700	38840	7	6700	38251	32
800	38764	7	3800	38833	8	6800	38219	32
900	38771	9	3900	38825	9	6900	38187	32
1000	38780	0	4000	38816	9	7000	38155	32
1100	38780	2	4100	38807	9	7100	38123	33
1200	38778	4	4200	38798	10	7200	38090	32
1300	38774	2	4300	38788	11	7300	38058	32
1400	38772	5	4400	38777	11	7400	38026	32
1500	38777	7	4500	38766	15	7500	37994	32
1600	38784	9	4600	38751	15	7600	37962	32
1700	38793	10	4700	38736	16	7700	37930	32
1800	38803	11	4800	38720	17	7800	37898	31
1900	38814	12	4900	38703	17	7900	37867	31
2000	38826	13	5000	38686	18	8000	37836	31
2100	38839	14	5100	38668	18	8100	37805	31
2200	38853	12	5200	38650	19	8200	37774	30
2300	38865	11	5300	38631	19	8300	37744	30
2400	38876	9	5400	38612	20	8400	37714	30
2500	38885	5	5500	38592	20	8500	37684	29
2600	38890	3	5600	38572	22	8600	37655	29
2700	38893	2	5700	38550	24	8700	37626	29
2800	38895	3	5800	38526	27	8800	37597	24
2900	38892	6	5900	38499	29	8900	37573	23
3000	38886	6	6000	38470	30	9000	37550	

METHANE (CH_4)

$CH_4 + 2O_2 = CO_2 + 2H_2O$; $\Delta E_0 = -345981$ B.Th.U./lb. mol

$T°$ F. Abs.	S		E		H		$H_p = H_v$	
400	42·153	1·618	2405	512	3200	710	345446	350
500	43·771	1·578	2917	691	3910	890	345096	201
600	45·349	1·477	3608	762	4800	960	344895	190
700	46·826	1·347	4370	811	5760	1010	344705	189
800	48·173	1·247	5181	861	6770	1060	344516	182
900	49·420	1·194	6042	927	7830	1126	344334	158
1000	50·614	1·155	6969	1004	8956	1203	344176	114
1100	51·769	1·118	7973	1077	10159	1275	344062	92
1200	52·887	1·086	9050	1148	11434	1347	343970	50
1300	53·973	1·055	10198	1215	12781	1414	343920	22
1400	55·028	1·030	11413	1284	14195	1482	343898	7
1500	56·058	1·007	12697	1350	15677	1549	343905	37
1600	57·065	0·987	14047	1417	17226	1616	343942	65
1700	58·052	0·968	15464	1480	18842	1678	344007	87
1800	59·020	0·943	16944	1546	20520	1745	344094	118
1900	59·963	0·929	18490	1612	22265	1811	344212	145
2000	60·892	0·915	20102	1678	24076	1876	344357	170
2100	61·807	0·903	21780	1742	25952	1941	344527	197
2200	62·710	0·891	23522	1805	27893	2004	344724	231
2300	63·601	0·879	25327	1868	29897	2066	344955	260
2400	64·480	0·868	27195	1927	31963	2126	345215	286
2500	65·348		29122		34089		345501	

ETHYLENE (C_2H_4)

$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$; $\Delta E_0 = -569936$ B.Th.U./lb. mol

T° F. Abs.	S		E		H		$H_p = H_v$	
400	49·236	2·610	2084	1070	2879	1268	568965	61
500	51·846	2·410	3154	1219	4147	1418	569026	131
600	54·256	2·210	4373	1331	5565	1529	569157	144
700	56·466	2·010	5704	1402	7094	1601	569301	123
800	58·476	1·840	7106	1459	8695	1658	569424	106
900	60·316	1·720	8565	1530	10353	1729	569530	109
1000	62·036	1·620	10095	1595	12082	1794	569639	113
1100	63·656	1·530	11690	1655	13876	1853	569752	118
1200	65·186	1·460	13345	1721	15729	1920	569870	130
1300	66·646	1·395	15066	1781	17649	1980	570000	135
1400	68·041	1·345	16847	1849	19629	2047	570135	148
1500	69·386	1·300	18696	1914	21676	2113	570283	164
1600	70·686	1·265	20610	1987	23789	2186	570447	186
1700	71·951	1·230	22597	2053	25975	2251	570633	199
1800	73·181	1·205	24650	2128	28226	2327	570832	229
1900	74·386	1·180	26778	2198	30553	2397	571061	251
2000	75·566	1·155	28976	2262	32950	2460	571312	266
2100	76·721	1·135	31238	2334	35410	2533	571578	293
2200	77·856	1·115	33572	2400	37943	2599	571871	323
2300	78·971	1·095	35972	2469	40542	2667	572194	353
2400	80·066	1·080	38441	2547	43209	2746	572547	390
2500	81·146		40988		45955		572937	

BENZENE (C_6H_6)

$C_6H_6 + 7{\cdot}5O_2 = 6CO_2 + 3H_2O$; $\Delta E_0 = -1362548$ B.Th.U./lb. mol

T° F. Abs.	S*		E*		H*		H_v		H_p	
400	0	3·831	0	1525	0	1724	1363312	428	1362915	527
500	3·831	3·788	1525	1885	1724	2083	1362884	336	1362388	436
600	7·619	3·735	3410	2228	3807	2427	1362548	259	1361952	358
700	11·354	3·675	5638	2557	6234	2756	1362289	196	1361594	295
800	15·029	3·611	8195	2870	8990	3068	1362093	90	1361299	190
900	18·640	3·543	11065	3168	12058	3367	1362003	28	1361109	71
1000	22·183	3·474	14233	3448	15425	3646	1362031	191	1361038	91
1100	25·657	3·403	17681	3715	19071	3914	1362222	248	1361129	149
1200	29·060	3·332	21396	3965	22985	4164	1362470	399	1361278	300
1300	32·392	3·258	25361	4200	27149	4399	1362869	504	1361578	404
1400	35·650	3·185	29561	4418	31548	4617	1363373	596	1361982	497
1500	38·835		33979		36165		1363969		1362479	

* Reckoned from 400° F. abs.

OCTANE (C_8H_{18})

$C_8H_{18}+12{\cdot}5O_2=8CO_2+9H_2O$; $\Delta E_0=-2207422$ B.Th.U./lb. mol

T° F. Abs.	S	Δ	E	Δ	H	Δ	H_p	Δ	H_v	Δ
400	99·644	7·933	9823	3372	10618	3570	2200830	1714	2203613	1021
500	107·577	8·404	13195	4423	14188	4622	2199116	974	2202592	278
600	115·981	8·576	17618	5376	18810	5574	2198142	422	2202314	271
700	124·557	8·300	22994	6026	24384	6225	2197720	148	2202585	549
800	132·857	7·973	29020	6578	30609	6777	2197572	103	2203134	799
900	140·830	7·826	35598	7229	37386	7428	2197675	474	2203933	1171
1000	148·656	7·418	42827	7582	44814	7781	2198149	626	2205104	1322
1100	156·074	7·341	50409	8235	52595	8433	2198775	948	2206426	1641
1200	163·415	7·034	58644	8585	61028	8784	2199723	1122	2208067	1819
1300	170·449	6·774	67229	8937	69812	9136	2200845	1242	2209886	1938
1400	177·223	6·602	76166	9290	78948	9488	2202087	1367	2211824	2060
1500	183·825	6·355	85456	9640	88436	9839	2203454	1505	2213884	2202
1600	190·180	6·123	95096	9893	98275	10092	2204959	1541	2216086	2237
1700	196·303	5·917	104989	10145	108367	10343	2206500	1570	2218323	2263
1800	202·220	5·633	115134	10196	118710	10395	2208070	1425	2220586	2122
1900	207·853	5·364	125330	10236	129105	10435	2209495	1258	2222708	1954
2000	213·217	5·165	135566	10362	139540	10560	2210753	1175	2224662	1868
2100	218·382	5·129	145928	10801	150100	11000	2211928	1416	2226530	2113
2200	223·511	4·992	156729	11003	161100	11202	2213344	1463	2228643	2159
2300	228·503	4·907	167732	11305	172302	11503	2214807	1598	2230802	2291
2400	233·410	4·832	179037	11608	183805	11807	2216405	1721	2233093	2418
2500	238·242		190645		195612		2218126		2235511	

TABLE OF $\frac{RT}{J}$ WHERE $\frac{R}{J}=1{\cdot}9869$

T° F. Abs.	$\frac{RT}{J}$	T° F. Abs.	$\frac{RT}{J}$	T° F. Abs.	$\frac{RT}{J}$
100	199	3100	6159	6100	12120
200	397	3200	6358	6200	12319
300	596	3300	6557	6300	12517
400	795	3400	6755	6400	12716
500	993	3500	6954	6500	12915
600	1192	3600	7153	6600	13114
700	1390	3700	7351	6700	13312
800	1589	3800	7550	6800	13511
900	1788	3900	7749	6900	13710
1000	1987	4000	7948	7000	13908
1100	2186	4100	8146	7100	14107
1200	2384	4200	8345	7200	14306
1300	2583	4300	8544	7300	14504
1400	2782	4400	8742	7400	14703
1500	2980	4500	8941	7500	14902
1600	3179	4600	9140	7600	15100
1700	3378	4700	9338	7700	15299
1800	3576	4800	9537	7800	15498
1900	3775	4900	9736	7900	15697
2000	3974	5000	9935	8000	15895
2100	4172	5100	10133	8100	16094
2200	4371	5200	10332	8200	16293
2300	4570	5300	10531	8300	16491
2400	4768	5400	10729	8400	16690
2500	4967	5500	10928	8500	16889
2600	5166	5600	11127	8600	17087
2700	5365	5700	11325	8700	17286
2800	5563	5800	11524	8800	17485
2900	5762	5900	11723	8900	17683
3000	5961	6000	11921	9000	17882

TABLE OF $\frac{R}{J}\log_e x = 1{\cdot}9869 \times 2{\cdot}30258 \times \log_{10} x = 4{\cdot}575 \log_{10} x$

x	$4{\cdot}575 \log_{10} x$	x	$4{\cdot}575 \log_{10} x$
1·25	0·4434	8·50	4·2521
1·50	0·8056	8·75	4·3097
1·75	1·1119	9·00	4·3656
2·00	1·3772	9·25	4·4201
2·25	1·6112	9·50	4·4731
2·50	1·8206	9·75	4·5247
2·75	2·0099	10·00	4·5750
3·00	2·1828	10·25	4·6240
3·25	2·3419	10·50	4·6719
3·50	2·4891	10·75	4·7187
3·75	2·6262	11·00	4·7644
4·00	2·7544	11·25	4·8090
4·25	2·8749	11·50	4·8527
4·50	2·9884	11·75	4·8954
4·75	3·0959	12·00	4·9372
5·00	3·1978	12·25	4·9782
5·25	3·2947	12·50	5·0184
5·50	3·3871	12·75	5·0577
5·75	3·4755	13·00	5·0963
6·00	3·5600	13·25	5·1341
6·25	3·6412	13·50	5·1713
6·50	3·7191	13·75	5·2077
6·75	3·7940	14·00	5·2435
7·00	3·8663	15·00	5·3806
7·25	3·9361	16·00	5·5088
7·50	4·0034	17·00	5·6293
7·75	4·0685	18·00	5·7429
8·00	4·1316	19·00	5·8503
8·25	4·1928	20·00	5·9522